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The Technological Importance of Accurate Thermophysical Property Information

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The Technological Importance of Accurate Thermophysical Property Information

Proceedings of a Session of the Winter Annual Meeting of
the American Society of Mechanical Engineers
Held in New York, NY, December 6, 1979

Editors:

Jan V. Sengers
Max Klein

Center for Thermodynamics and Molecular Science
National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

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American Society of Mechanical Engineers
345 E. 47th St.
New York, NY 10017

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FOREWORD

This publication contains a series of papers presented at a session of the Winter Annual Meeting of the American Society of Mechanical Engineers held in New York, N.Y., December 6, 1979. The session was organized by the Committee on Thermophysical Properties (Committee K-7) of the Heat Transfer Division of the ASME. The mandate of this committee is to encourage scientific research in the field of thermophysical properties and to facilitate the flow of information from science to engineering so as to provide the engineering community with an adequate base for thermophysical property information.

Of particular concern to the committee are the complications that arise from lack of communication between the users and generators of thermophysical property information. The user may have access to a computer program yielding thermophysical property values, but often does not know to what extent this information is reliable. As a consequence the technological decisions may unknowingly be affected by a lack of accuracy of the thermophysical property information used in the analysis.

To call attention to these problems, the committee organized a session devoted to a discussion of the importance of accurate thermophysical property information for technology. The committee is convinced that this issue deserves wider recognition in the engineering community and expresses its appreciation to the National Bureau of Standards for its willingness to publish the proceedings of the meeting.

Jan V. Sengers, Chairman
Committee K-7
Heat Transfer Division, ASME

ABSTRACT

These papers were presented at a meeting of the American Society of Mechanical Engineers. The meeting session addressed the role of the accuracy of thermophysical properties data in a number of applications areas. The areas covered included aerospace sciences, where such data have played a central role for a number of years; and geosciences, where first steps are being taken toward using accuracy in describing systems in terms of thermophysical properties. Also included were a discussion of the economic value of accuracy in the chemical process industry, a description of the role of data centers, and a description of several high-quality data compilations. An example of a specific problem in the design of a heat exchanger for geothermal applications was also presented with the design uncertainties produced by data in accuracies illustrated.

KEY WORDS

Aeroscience; data accuracy; design; geothermal; process; thermodynamics; transport properties.

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The Role of Data Accuracy in Applications of Thermophysics: An Introduction and Overview

Max Klein
Thermophysics Division,
Center for Thermodynamics
and Molecular Science,
National Bureau of Standards,
Washington, D.C.

The importance of thermophysical properties data to technology and to society is described. Arguments are presented for a rapidly growing importance for the role of the accuracy of such data. Specific examples are presented of instances where an economic value has been placed on typical uncertainties in such data.

INTRODUCTION

This session has as its essential purpose an examination of the need for accuracy in thermophysical properties data. By the thermophysical properties of a system, we mean those properties which measure the response of the system to thermal and mechanical stimuli. These include both the thermodynamic properties (which describe the change of the system between initial and final equilibrium states) and the transport properties (which describe the flow of heat or material resulting from a steady departure from equilibrium). The speakers will describe the role played by the accuracy of the thermophysical properties data used in their research areas. This will be done by them both through historical examples and through typical engineering calculations. The research areas associated with these papers include what can be called an area of mature users of accuracy in thermodynamics (in the sense that their need for accuracy has been well established for a number of years). Our example of this is from aerospace science. Included also is an instance of awakening users of accuracy in thermodynamics (the chemical process plant design users on whom pressure for accuracy is being applied due to rapid escalation in cost of energy and material) and an instance of new users of accuracy in thermodynamics (the geophysical sciences, whose models and computational tools are only beginning to be able to use well-defined thermodynamic and transport property data of some reliability).

In this introduction, we shall attempt to give the flavor of the importance of thermodynamic data to science and technology and shall indicate the growing role played by their accuracy. Our emphasis will be on the role of fluid properties in process plant design. Specific applications in several other broad areas and in greater detail will be presented by the individual session speakers who will also discuss transport properties.

The science of thermodynamics deals with the flow of energy; it deals with relationships between heat and work as forms of energy and especially with the efficiency of the interconversion of various forms of energy. This can be taken to mean that thermodynamics is that science which studies the effective conversion of energy into useful work and vice versa.

The breadth of applicability of thermodynamics is widely recognized. Its use in analysis and design in the physical sciences and engineering is ancient on the time scale of scientific advances. In recent decades, there has been a rapid escalation in applications of thermodynamics stemming from the fact that the flow of energy as heat and work has now become necessary for the very existence of civilization and of life itself. In our own society, the increase in the flow of energy in the last hundred years has been directly responsible for a major increase in the productivities of labor and capital, resulting thereby both in an effective and productive modern technology and in a major increase in our standard of living.

Among the applications of thermodynamic data are those which are direct and of obvious technological use. These applications occur in the design of chemical process plants, electric power generating systems, natural gas processing plants, oil refineries, etc. There are, in addition to these purely technological uses, applications which can be classified in a language appropriate to elucidate social impact. A recent publication (1)* contains a list of social problems to whose solutions thermodynamics contributes. Although most of these are applications of technologies whose system designs are in turn based on thermodynamic data (and are, so to speak, dependent on such data in second order), those data nevertheless play a central role in the design of the means for solving the problems indicated. The social problems listed include the

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*Numbers in parentheses in text in each paper refer to references at the end of that paper.

"-Maintenance of the quality of the air we breathe and the water we drink, and the integrity of our natural resources of land and water;

-Production, distribution, and consumption of food and of energy;

-Proper disposition, and recycling where possible, of the waste produced by humans in the home, in factories, on the farm, and in recreation;

-Proper disposition and use of the thermal discharge from fossil fuel and nuclear power plants;

-Problems of transportation, local, national, and international, by land, water, and air;

-Problems of communication, local, national, and international."

In addition, thermodynamics contributes to the design and maintenance of health care facilities and even sometimes provides models for understanding biological systems (2).

Thermodynamics is not only necessary for solving the above problems, but is also needed for doing it efficiently, a concept becoming of primary importance to our society. The escalating growth in dependence on energy and synthetic materials in the last decades has caused almost all aspects of human life to be dependent on systems designed with the use of thermodynamics (as the list above indicated). As the demand for energy and synthetic materials approaches the limit of availability of the raw materials involved, our lives begin to depend on small differences in the efficiencies of those systems and hence on the accuracy of their designs. As relates to energy, it has been suggested (3) that, in order to "stretch out our sources of energy, and to make a given unit of energy do its maximum for use, we need to analyze every significant process and reaction associated with human activity in the world and see that such activity is carried out under conditions that yield a maximum of thermodynamic efficiency." The realization of this has, in fact, even led to recent Congressional legislation which directed certain Government agencies to undertake a study of the methodology of thermodynamic efficiency calculations (4).

As relates to materials, it is clear that the direct effect of material shortages on the economy can be devastating and that accurate thermodynamic data can play a large role in reducing such shortages. For example, a study made by the A.D. Little Co. during the aftermath of the oil embargo projected a loss of 1.6 million jobs across U.S. industry if feedstock supplies (mainly petrochemical) were reduced by only 15% (5). More efficient use of such feedstocks obviously, then, will have a direct economic effect on the Nation. A specific example of this and one in which the potential role of accurate data is apparent can be found in the feedstock situation for ethylene. A major part of the raw material supply for the petrochemical industry consists of ethane, propane, and heavier raw materials extracted in natural gas processing plants. These materials account for three-fourths of the ethylene produced in the U.S., almost half of which is derived from ethane. The production of these feedstocks is declining, however. Yet bigger supplies are available as indicated by an industry executive who stated that (6), "At present, about 85% of the ethane in domestic natural gas is not recovered and is burned as fuel. The recovered portion could easily be raised from the existing 15% to somewhere between 50 and 70%. In the same way, the percentage of propane extracted from gas could be increased from the present 50% to between 75 and 90%." Increased efficiencies in natural gas processing can thus lead to material conservation and could play a major role in determining and lowering what could otherwise become an unbearably high price. Such increased separation efficiencies depend strongly on the quality of the thermodynamic data used in process designs (7).

Clearly, then, thermodynamics plays an all pervasive role in our society and the accuracy of thermodynamic data affects our daily lives through its effect on the efficiency of energy and material usage. Yet, despite this, support for research in thermodynamics has been noticeably drying up. Concern from within the field at the rapid reduction in the number of research laboratories and in the number of graduate theses published has been vociferous (8). Yet this has not generated a shift in resources to reverse this trend. The reasons for such an apparent contradiction (i.e., between an obvious and growing strong national need for accurate thermodynamic data and a lack of resource support) are not obvious. Among possible reasons are the following:

Thermodynamics is based on two very general laws which are totally independent of the properties of any particular substance. This is at the same time the power of the discipline and a reason why its utility is often not understood well. Thermodynamics, of itself, has nothing to say about particular substances and is, in fact, nothing more than a "bare boned" computational framework until the properties of particular substances are introduced. However, it becomes an extremely powerful tool when good data are available, producing an efficiency in the use of property data which can be truly awesome (9).

Surprisingly enough, the need for accurate data is not always understood. That need is often clouded by the successes in the use of thermodynamics for those systems (often the ones used in textbook examples) for which accurate data do exist. Because of the breadth of its applicability, success with thermodynamics in one research area can lead to a feeling of guaranteed success in other similar areas. This leads to a sense of false security according to which it is assumed that success will be waiting when needed. This may in turn remove the pressure for program managers to support the taking of such data, especially where the application lies in the future.

Adequate support for thermodynamic data development might also be absent because of the structure of the measurement "system" for such data. By that system is meant the sum total of all measurements, theories and correlations which produce tables or mathematical representations of thermodyanmic data. Measurements required for producing accurate thermodynamic property data are difficult and tend to use classical methods of measurement. Experiments require extremely careful design and painstaking attention to detail. The measurements are, furthermore, time consuming. Such measurements are rarely in response to an immediate technological need because the time needed is generally several times that available for the solution of a technological problem. As a result, such measurements are rarely carried out in industrial settings. Since the measurement methods tend to be classical and the time scale long, it is also rare that such measurements can be made the basis for a graduate thesis. Even when they can be, the tendency must be for the measurements to be divided among several students in time sequence with some loss of continuity. It is therefore only in the nonprofit and government laboratories that the required measurement programs can possibly be designed properly and carried out. The advent of a strong emphasis on short term relevance at those laboratories, (perhaps in emulation of the industrial laboratory) has made it difficult to support such programs even there. Thus support for the accurate measurement of thermodynamic properties has tended to be left without a natural sponsor. In fact, managers in the various parts of the system tend to think the data they will need are actually being compiled in another part of the system and are shocked when the data are not on the shelf when urgently needed.

The lack of sufficient support for thermodynamic measurements has often led to a "band-aid" approach to the production of thermodynamic data in which measurements are made only as an immediate need for them is discovered. Because of the aforementioned long time scale, however, only the very minimum amount of data can generally be taken and most often at relatively low accuracy. This has resulted in a literature replete with isolated data on various substances and mainly with very poor accuracy. This has, in the past, fortunately not resulted in a major industrial bottleneck since, until recently, the fuel and material required in technological and societal applications of thermodynamics have been easily available as well as inexpensive. Hence efficient use of energy and materials has often not been a major concern and the attainment of the highest accuracy has rarely been a major driving force in the designs of the system involved. In other words, the economic value placed on accurate and consistent thermodynamic data for various substances has not been sufficiently high to produce a large industrial demand for data of such quality. This situation is rapidly changing with demands now being voiced for designs based on thermodynamic data of the highest accuracy. There are several reasons for this change.

Recent events have produced a dramatic awareness of impending shortages and of associated increases in costs (both artifical and natural) in energy and materials supplies. Demands for accurate data are also accelerating because advancing technology now produces individual plants of very large capacity. This makes the economic payoff for better designs highly significant even in the design of a single plant. In the case of ethylene producing plants, for example, there has been an eight fold increase in plant size for new plants in the last decade and a half (10). There has been a corresponding increase in capital cost for individual plant construction. Overdesign has, therefore, become very costly in capital cost, in feedstock cost and in energy cost. A more subtle additional reason for needing accurate data comes from the strong legal requirements for minimizing the environmental impacts of technological processes, requirements which include the need to file detailed statements of expected environmental impact in advance of plant construction. This places strong demands on design predictability. It is obvious that trace elements of toxic materials in the output of a huge plant can produce large quantities of environmentally unacceptable material even though such quantities are only a small (and even trivial) percentage of total material output.

The demand for accurate data generated by the pressures of environmental considerations is often for producing alternative designs, especially those calling for tight control over waste energy and particular effluent materials. These call for very accurate data. Waste energy and material come out of large processes as small differences between large numbers, i.e. the differences between the large amounts of energy and materials flowing in and the almost equally large amounts used up in the processes. For example, a particular plant which makes one million pounds per day of ethylene and a lesser amount of propylene produces as waste having a potential detrimental environmental effect, 700 pounds per day of solid material (11). Although this is a very small difference between the almost two million pounds of input material and the almost two million pounds of output material, (*representing only several parts in ten thousand of the material flow*) it is nevertheless enough to cause environmental problems.

I have tried, up to this point, to establish the broad utility of thermodynamic data to technology and to our daily lives. I have also attempted to indicate why, despite this, there has not been pressure for producing the required large amounts of such data. I have indicated why this is changing and, in fact, why there is a growing need not only for data but for *accurate* data. In what follows, I shall give a small number of specific examples in which the need for accurate thermodynamic data is clear. In some cases, the detrimental effects of the use of inaccurate data are presented.

THE ROLE OF ACCURACY

Accuracy plays an important and obvious role in scientific applications of thermodynamic data. There, in each application, data inaccuracies place a limit on the measurement accuracy obtainable. More important in the national scheme of things is the role of accuracy in technological applications. We have already indicated that applications of thermodynamic data are all pervasive in our economy and in our daily lives and that the importance of accuracy, though limited until recently, is rapidly increasing.

In most technological applications to which we shall refer, thermodynamic data are used in plant and system design. In design, the data play an initial role in establishing the feasibility of a project. Once feasibility has been established, the data play a most important role in attaining adequate process efficiency. The economic impact of accuracy in the feasibility role can be quite large, the worst case being one where available (and inaccurate) data show a process to be feasible but where the inaccuracies are such that the completed plant either does not work or turns out to be uneconomical to operate. Written examples of this are hard to find, for obvious reasons, but anecodotes do exist outside the published literature. A more usual case is one in which inaccuracies increase capital costs and/or reduce operating efficiencies unnecessarily. The effect of data inaccuracies on systems operating efficiency can be documented quite easily by using computer models. Surprisingly enough, such calculations have been rare. The fact that their number is growing, however, attests both to the increasing importance of data inaccuracy considerations in design and to the ability of the designer to use data of greater accuracy than is presently available to him. Times have changed drastically in this regard. Thus, in a book on design strategy (12) it is pointed out that "in the past the accuracy of data was on the same order as the accuracy of the methods of computation. Now the numerical accuracy of the mathematics often far exceeds the accuracy of the basic data upon which the mathematical equations are based." This says that the tools available to the engineer are now waiting for more accurate data. These tools are so good that, given a sufficient data base to describe the behavior of the materials used, the latest computer models for plant processes can be used to design plants with fewer (and, in principle, even with no) pilot plant stages. One can, in fact, use the combination of models and data after a plant is operational to perform dynamic optimizations of plant parameters (13). The hardware already exists (and development rapidly expanding) even for using microcomputers which are small enough for inclusion in run streams and which are yet powerful enough to solve quite complicated mathematical models for process operations. An example is the development of microprocessors for the control of automobile engines (14) and those for control of industrial and consumer combustion processes. The hardware and software technology for this is far ahead of the quality of the data available. This is an instance where available technology is far ahead of the kind of fundamental knowledge that it can already use. This situation faults the technological community for lack of foresight and long range planning.

We have indicated that thermodynamic data are important to science and technology and that their accuracy plays a rapidly expanding role in the national scheme of things. A prime example of what can be done by industry with adequate data "on the shelf" at the time of need is given by the petroleum industry in the U.S.A. This industry became the beneficiary of much basic data on the thermodynamic, thermochemical, physical, and spectroscopic properties of hydrocarbons, beginning before World War II and continuing about 20 years. With these data, the petroleum industry was able to develop an almost magical power to determine the optimum conditions of temperature and pressure for carrying on its many different refining operations involved in the production from petroleum of its numerous important products for man.

THE SIZE OF THE DATA GATHERING PROBLEM

Now that we have examined the role in our society of thermodynamics and have indicated the need for accurate thermodynamic data, let us look at the size of thermodynamic data gathering problem. The number of material systems of potential technological interest is quite large as are the number of potentially useful properties of each such system. The total data set required is, in fact, staggering. It has been suggested that *for the design of energy plants alone, for each material system of interest*, (15) "thermodynamic and related properties would need to cover, as appropriate in specific cases, temperatures from 10 degrees absolute (10 K) up to about 5000 degrees absolute (5000 K). Similarly, for appropriate systems, measurements would need to cover pressures up to several hundred atmospheres." This range of variables could not be spanned with less than one or two thousand data points *per property per system of interest* - too many points to measure. Thus the data needs are large. These needs are also, in a real sense, unpredictable. Thus, with the exception of those very few substances whose utility is broad and long term, e.g. steam, the probability is quite small that a need will exist at any given time for some particular subset of thermodynamic properties for a particular substance or mixture chosen at random. On the other hand, at any particular time, the probability is quite large that a need exists for thermodynamic data of some kind for some substance and that this need was not previously predictable. Large unpredictable needs of this kind require the development of an easily accessible data bank containing properties data for many substances.

It is hard to develop resources to take care of such large but unpredictable data needs. There are those who would respond to such a task through measurement programs for producing data as needs arise. Unfortunately, the time scale for producing laboratory data is quite long, even where the needed measuring apparatus already exists. A "response by measurement" approach is therefore inadequate since it would frequently produce data only after the need for them had been satisfied in some less efficient manner. The only sensible approach would involve a program for accumulating a bank of data in advance of need for all systems of possible interest. If a purely measurement approach is used for this, technology predictions would need to be combined with long range goals to anticipate needs far enough in the future to have data "on the shelf" when needed. Even where this can, in principle, be done there are problems because of the enormous amount of data which could be of potential interest.

The only realistic solution to this problem requires the development of *predictive* models which make use of a very small number of data points for each material system, these data being necessary to determine values for parameters contained in the models. The use of models and intuition for estimation of data is a fairly advanced art in reaction thermochemistry where the development of models is almost as old as modern chemistry itself. Thus it is estimated (13) that a majority of the entries in the American Petroleum Institute Task 44 publications are estimates based on models. Model development for thermodynamic properties of non dilute phases has been slow and mostly empirical mainly because of the absence of adequate theories for the dense fluid and for mixtures as well as the inadequacy of the accuracy of much of the data base.

THE ECONOMIC BENEFITS OF MORE ACCURATE DATA

The potential economic leverage to be obtained from resources applied toward achieving more efficient production of basic materials from petrochemical processes can be gauged from the various uses to which a product is put. Take ethylene as an example. Table 1 contains a representative list of ethylene uses generally not carried to final end product and indicates the broad economic impact more efficient designs of systems which use ethylene can have. It should be realized, of course, that the direct dollar effects of improved ethylene data are quite small as a percentage of the quantity of ethylene converted and therefore not a simple matter to document. Nevertheless, the breadth of the applications for ethylene multiplies this small effect by a huge number resulting in a very large total dollar effect relative to the cost of any data gathering program. This makes for considerable cost effectiveness leverage for any resourses expended in improving such data.

Economic payoff of accurate data can also be expected because of the extensive distribution of small energy conversion systems (with the automobile and home heating units being prime examples). Thus, for example, a small increase in the energy conversion efficiency of the automobile would have a very large national effect on the use of energy and of petroleum

Table 1: Representative Uses for Ethylene

	PRIMARY DERIVATIVE	CHEMICAL INTERMEDIATE AND END PRODUCTS			
		Di & Triethylene Glycol		Urethane Foams	
				Solvent Extraction	
				Polyester Resins	Alkyd Coatings
					Foams, Fibers & Film
		Ethylene Glycol		Antifreeze	
	ETHYLENE OXIDE	Nonionic Surfactants	Synthetic Rubber	Hydraulic Fluids	Plasticizers
		Acrylonitrile	Plastics	Polyethylene Glycol	Lubricants
			Synthetic Fibers		Emulsifiers
				Plasticizers	
				Detergents	
		Ethanolamines		Cosmetics	
			Jet Fuel Additives	Textile Chemicals	
		Glycol Ethers	Solvent	Gas Scrubbing	Latex Paints
					Adhesives
				Polyvinyl Derivatives	Textile Finishing
		Solvent			Coatings
	ETHYL ALCOHOL	Toiletries			Molding Compounds
		Acetaldehyde	Chemical	Acetylsalicylic Acid	Aspirin
		Pharmaceuticals	Intermediates		2,4-D & 2,4,5-T
				Chloroacetic Acid	
			Tires		Weed Killers
		SBR Rubber	Footwear	Cellulose Acetate	Rayon & Film
			Gaskets		Lacquers
ETHYLENE			Film	Other Esters	Solvents
	STYRENE MONOMER		Foams		Plasticizers
		Polystyrene Resins	Paneling		Jet Lubricants
			Wall Tile		
		Anesthetic			
	ETHYLENE DIBROMIDE	Refrigerant			
		Lead Scavenger(TEL)			
		Ethylene Diamine	Solvent	Wire Insulation	
	ETHYLENE DICHLORIDE		Stabilizers	Garden Hose	
			Polyvinyl Chloride	Flooring & Sheets	
		Vinyl Chloride	Refrigerant	Rainwear	
		Tetraethyl Lead	Gasoline Additive	Upholstery	
	ETHYL CHLORIDE		Paper Coating	Shower Curtains	
		Ethyl Cellulose	Lacquers		
			Packaging		
	ETHYLENE-PROPYLENE COPOLYMERS	Rubber Specialties			

products. It has been estimated (14) that (as of the end of 1974) "each one percent increase in auto engine combustion efficiency saves about 14.5 million barrels of oil per year which saves this nation over 150 million [1974] dollars per year in balance of payments. [and] this example of payoff [is] conservative ... ."

We have already pointed out that published calculations of the effect of uncertainties in thermodynamic data on plant feasibility and operating efficiency have been few. It is only fair to point out that in many situations apparent economic effects of data uncertainty are not simply related to plant operating economics. Uncertainties in the data can be over-shadowed by large uncertainties in the design and operating characteristics of mechanical components, in variations in feedstocks or in other variables not directed related to the original design requirements. In such cases the "actual" effect of data uncertainties can be negligible (except insofar as a component of excessive size is used as a direct result of the data uncertainty). In certain special cases, the effect of uncertainties can be a strong function of an operating parameter whose nominal value is either initially very hard to predict or is entirely dependent on the design of other components. Figure 1 taken from page 337 of reference (12) illustrates such a situation. When the cooling water turns out to be needed at the temperature designated A, the effect of data uncertainty on the design is negligible. When temperaature B is needed, the effect of the same uncertainty

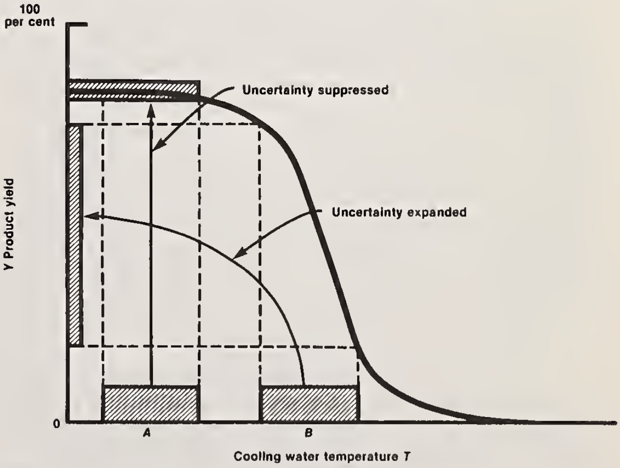

Fig. 1. Propagation of uncertainty through a design.

in the data is large and is, in fact, an amplified version of the original uncertainty.

EXAMPLES OF THE EFFECT OF DATA UNCERTAINTIES ON PLANT COSTS

Perhaps the first detailed estimate of the economic effect of data uncertainty was published by Baker (16) almost two decades ago. This carefully reasoned paper had very little effect on research support. There are those who take this to reflect faults in our engineering educational system and find it to be symptomatic of an uneasiness which most operating engineers feel with thermodynamics. More likely, however, this reflects the historical low cost of energy and raw materials. In either case the study by Baker had very little apparent impact. More recently there have been some attempts at documenting more extensively (if with less detailed use of economics) the cost of data uncertainties. We have collected a small number of illustrations of such calculations.

The examples we have collected are mainly (but not all) hypothetical and/or anonymous. They are, however, based on solid engineering procedures and hence are representative of actual situations. The specific examples used by us should not be taken as being the most typical or as even being illustrative of the most important situations. Our choice has depended on the availability of these examples and on the fact that they do illustrate problems which engineers frequently meet. The examples are used to illustrate the economic value of uncertainties in the data where such a value is easily calculated. These are not examples of underdesigns which would lead to plant failure or to drastic retrofit. Such extreme examples are generally unavailable in the literature for obvious reasons. Situations have also not been included in which the "safest" design (generally also the most expensive) does not work, nor have we included estimates of the cost of reduced reliability resulting from component overloads which result from corrections for low yields. In the following we have separated our examples into property and utility categories. In most instances we simply indicate the conclusions of the author and leave it up to the reader to go to the original paper for details.

1. Retrofitting -

A paper by Squires and Orchard (17) illustrates the problems met in "retrofitting" gas processing plants to correct for missing a plant design point as a result of data uncertainties. In their first example, use of inaccurate K values for methane resulted in reduced propane recovery from the stream. The method used to correct this led to higher power consumption and extra cooling tower duty cycle. A second necessary correction resulted in a reduction in the rate of removal of ethane in the early stages of the stream. Thus lower efficiency of plant operations at a higher operating cost had to be accepted in the retrofit.

2. Critical parameters -

Critical parameters are most widely used in corresponding states representations of P,V,T surfaces (18). Such representations are among the best computational tools available to engineers especially for predicting data for substances on which experimental measurements have not been made. Corresponding states correlations, however, are only approximately based on fundamental notions. Since the basic researcher has not yet been able to produce an alternative of reasonable accuracy and ease of use, corresponding states methods will continue to be used by engineers for some time. Perhaps the most widely used corresponding states representation is one in which the critical parameters are used as reducing variables. Generalized charts of such reduced representations have been available for some time (19). The need for good critical parameter data for using these representations can be gaged from the effect of uncertainties in engineering methods used to estimate the parameters (20). It has been estimated (21) that at the limits of accuracy for such predictions, specific heats are obtained from the generalized representations which can be in error by 25%. Such errors in specific heats can result in a construction cost difference of $600,000 (1960 dollars and plant size) in the design of a gasoline plant and in an increased cost for the gasoline produced.

3. Vapor pressure -

Vapor pressures are among the most useful of thermodynamic data. Obvious examples of their utility are in safety calculations and in predictions of relative volatility which, in turn, are needed in the design of fractionators. Zudkevitch (22) includes an interesting study of the effect of vapor pressure errors, at the state of the art of engineering correlations, on the cost and operating characteristics of a process designed to remove 97% of the isopentane from a naptha stream. (Isopentane has been used to increase the octane rating of gasoline thereby reducing the amount of lead additive required). He found a spread in capital investment of $65,000 (1968 dollars) in a nominal cost of $550,000 for major equipment, a difference of approximately $100,000 (1968 dollars) in a nominal $400,000 investment in energy generating equipment and a difference of $100,000 per year (1968 dollars) in a design value of $450,000 in operating expenses. In addition, he estimates that the design which uses published data at one extreme of their range of uncertainty would probably not work well enough to be satisfactory and so would require expensive plant modification after a period of unsatisfactory process yield.

4. Volumetric properties -

Volumetric properties have many scientific and technological applications especially in those thermodynamic calculations which require the equation of state. However, our examples are drawn mainly from applications in the sale of large quantities of fluids (i.e. custody transfer). Uncertainties here produce an uncertain market and can destroy equity between buyer and seller in the market place. When the market occurs at a national boundary, such uncertainties can contribute to uncertainty in the value of currency transfer between nations.

a. Custody transfer contracts for natural gas are based on heating value (in BTU). Actual transfer is based on composition and quantity of material. The latter is measured by a flowmeter which measures pressure, temperature and flow rate. These are converted to quantity of material through the use of an equation of state. Based on estimates of the state of the art and on an arbitrary choice for the cost of natural gas, Zudkevitch estimates that uncertainties in LNG density at the time of his publication would result in an uncertainty of $15,000. in the transfer of the custody of the contents of a typical LNG ship. If the U.S. eventually imports LNG from 500 such ships annually, the annual uncertainty begins to approach $8,000,000. (Actually more at 1979 gas prices).

b. The critical point of ethylene is approximately 9.5°C. This is close to winter ambient conditions in the Houston area where most custody transfers of ethylene take place. Temperatures near critical are therefore sometimes "natural" ones for the custody transfer of ethylene. Properties of ethylene have been very poorly known (23) even several degrees above the critical temperature making custody transfer at such temperatures very uncertain. For this reason, many custody transfer contracts call for the fabrication of a steam plant at the metering station, for the sole purpose of heating the ethylene to a temperature where (generally arbitrary) agreement can be reached between buyer and seller for its properties. Such a steam plant costs approximately $30,000 (1970 dollars) to build and requires continuous energy generation. After the ethylene has passed through the flowmeter and custody transfer has been effected, its temperature is returned to its original value. On several occasions, as a result of steam plant failure, because of the particular adiabatic path dictated by the steam plant design, the ethylene temperature and pressure settled into a state very close to critical. Because of very large uncertainties in data correlations near the critical point, the resulting error estimate for the metering process as to quantity transferred approached total uncertainty (24).

c. To take care of supply and demand fluctuations, ethylene is often delivered to temporary salt dome storage through a custody transfer arrangement. As a test on the accuracy of the custody transfer process, one such salt dome was completely evacuated by its owners and the amount of ethylene removed measured. Comparison with company records indicated that the metering process showed much *more* ethylene had been removed than had been stored, a clear indication of the inadequacy of the process used for conversion of flow parameters to quantity of material (25)! Since the equation of state plays a key role in that process, this is a clear indication of the inadequacy of the basic thermodynamic data for ethylene.

d. A knowledge of volumetric properties is also required in the design of compressors. Zudkevitch illustrates the effect of data uncertainty on the design of the ethylene compression stage in a hypothetical polyethylene plant. Compressor design uncertainty in that case could lead to a 10% cost uncertainty resulting from overdesign of a compressor (an uncertainty of roughly $100,000 1974 dollars). When the error leads to an underdesign, potential serious operating problems involving equipment overloads could result. Since such plants are designed for continuous service with large continuous input of feed stock, shutdowns are very serious and costly. Zudkevitch also points out that ethylene is a fortunate example because he considered its properties to have been among the best known! The larger uncertainties for other substances *and especially for their mixtures* could lead to very costly errors indeed.

5. K values -

Except under unusual circumstances, a liquid mixture in equilibrium with its vapor has a different composition than its vapor. The ratio of the concentration of a particular component in the vapor phase to that of the same component in the liquid phase is defined as the K value of that substance in the particular mixture at the temperature and pressure of interest. Knowledge of the K values of the constituents of a particular mixture are obviously important in the design of plants in which certain species are to be removed from that mixture. In fact, the ratio of the K values for two constituents in a mixture is a good measure of the ease with which these two are separated and hence of the economics of the separation process. Albright (25) has examined the implications of uncertainties in K value data on the separation of ethane from methane, a process which is important to the natural gas industry (see introduction). In addition to pointing out the dangers inherent to the extrapolation of such data, Albright presents several specific examples. Using two popular correlations for K values, he obtained an uncertainty of 41°F in the calculated bubble point. A large difference in refrigeration cost between the two extreme designs resulted. An indication of the cost of this uncertanity can be seen in another example given by him in which there was an uncertainty of some 3°F in the predicted bubble point. In the latter case, an additional 12,000 horsepower of compression (and possibly an additional stage of refrigeration) was required with a difference of $1,000,000 in the cost of capital equipment! In yet another illustration described by Albright, involving the recovery of propane from natural gas, there was an uncertainty of $200,000 in refrigeration equipment.

The paper by Squires and Orchard (17) already mentioned above as containing examples of the cost of retrofitting contains two examples of the effect of K-value inaccuracies on the operation of actual gas processing plants. In one plant, the use of inaccurate methane K-values resulted in corrections which caused there to be higher fuel gas consumption (17%), higher steam consumption (29%), higher cooling tower duty cycle (30%) and higher electrical power useage (17%). In addition, ethane recovery was reduced. In a second plant cited in the paper, the use of inaccurate K-values was shown to be the cause of considerably reduced propane recovery.

6. Enthalpies -

In 1960, Ovid Baker of the Socony Mobil Company published a very careful economic analysis of the effect of uncertainties in thermodynamic data on the cost of capital equipment and on operating costs in petroleum refineries (16). Restricting himself to effects on the cost of heat exchangers in refinery and natural gas plants, he found that uncertainties in enthalpy correlations resulted (in terms of 1960 economics) in an annual cost of $2,300,000 provided one restricted the error in sign so as always to produce overdesigns. Obviously, errors which produce inadequate designs would be more costly in terms of reduced yield (per dollar of total investment) and in terms of the high cost of design modification for retrofitting completed plants in order to make them work better or at all. Baker also considered the cost per barrel of output of overdesign in refineries and obtained an estimate of roughly $4 (in 1960 dollars and at 1960 oil prices) per barrel of new capacity!

7. Liquified natural gas -

Problems in operating a natural gas liquifier arising from inadequate data were discussed in a paper which appeared in 1973 (26). We present a number of direct quotes from that article. The need for easily useable and accurate correlations is clearly stated. Italics are used by us for emphasis.

"...the lack of sufficient thermodynamic data and the absence of computer programs forced the designer to choose the most conservative solution.

Although a high operating pressure was desirable, it was limited to 39.5 atm in order to more closely design the distillation columns removing the C_5 and heavier hydrocarbons, particularly the aromatic components which tend to freeze up at these temperatures. Data were not available during the design stages to safely consider operation above 40 atm. Actual performance of the distillation column at a pressure of 43 atm proved that calculation procedures were not only conservative but that separation at higher pressures was highly feasible. This higher operating pressure was necessary to correct a vapor-liquid equilibrium error which was discovered at the end of the natural gas condensation curve for conditions of about 1.5 atm at constant temperature. *This error was due to a lack of information concerning the exact behavior of helium (0.2% mol) in a hydrocarbon mixture which also contains 6 mol% nitrogen.* At the original design pressure, natural gas condensation was not completed in the ethylene cycle and was therefore carried through to the first step of the methane cycle, resulting in a cycling steam flow rate for the turbocompressors with a corresponding instability of the complex steam cascade. The solution to the problem was found simultaneously but independently by the plant operator and the process designer who had tested, by then, the actual behavior of helium. The appropriate increase in pressure determined by both was found to be equal.

In order to minimize internal plant gas consumption, maximize LNG production, and provide for a five-year payout on marginal investments, a minimum-power-consuming plant was required. *The choice of cold suction compressors, which appeared to meet these conditions, was the result of hasty decisions primarily because of the slowness of hand calculations.* Actually, atmospheric temperature suction compressors would have resulted in a lower overall power consumption but would have required a greater heat transfer area for the heat exchangers. The power distribution between the compressors for this case would have been better balanced and startup procedures would have been greatly simplified. Furthermore, connecting and interconnecting piping could have been uninsulated carbon steel. *The choice of the cold suction compressors was greatly responsbile for the very high piping and insulation costs, which reached 50% of the investment in the liquifaction units area.*

The lesson learned from this design and the resulting operational experience was that a major effort in fundamental research was required in the area of hydrocarbon thermodynamics covering a temperature range from ambient down to -265°F for pressures from atmospheric up to 100 atm, with particular emphasis on the liquid-vapor equilibrium of complex mixtures."

THE SESSION PAPERS

We now turn to the contributed papers. This session includes papers ranging from a research area in which the need for accurate thermodynamic data was well established years ago to one in which the concept of a need for accurate data is only just beginning to be felt and with other areas between. The subject areas selected could only be representative due to time constraints. An exhaustive examination of areas in which accuracy in thermophysical properties plays an important role would have required several days filled with papers. Running through all the papers is a message that a need for more accuracy already exists and that this is rapidly becoming urgent.

It is interesting to note among the various papers the interplay between the ability to use more accuracy and the drive for such accuracy. Thus in the 1950's the appearance of much improved molecular correlations for certain fluid properties so satisfied the needs of the times that pressure for improvement abated (27). The time has again arrived where the ability to use accurate data has been developed far beyond the accuracy of the available data. Because of a strong pressure for energy and materials conservation and for the maintainance of environmental integrity, there is a strong need for committing national resources toward remedying this inconsistency. This session's papers present strong arguments for this.

Also running through the session is an indication of a strong need for close coupling between the producer of accurate data and the user of such data. This would ensure the use of the best data by user and would enable the user to have some understanding of limitations and uncertainties in the data.

REFERENCES

1 Rossini, F.D., "Conference on Thermodynamics and National Energy Problems," June 10-12, 1974, National Academy of Sciences, Washington D.C., p.5.

2 Professor Schmidt-Nielsen, Duke University, private communication referring to the use of the Stirling cycle for describing the metabolic cycle of a particular desert mammal.

3 see reference 1.

4 Public Law 95-619, National Energy Policy Act, Title VI part 5, section 683, (1979).

5 Quoted in Bissinger, F.L., "Changing feedstocks - chemicals or calories," Chem. Eng. Prog. 71, p. 30-33 (May 1975).

6 Bissinger, F.L. - see reference 5.

7 Private communications from several process design engineers on the staffs of large natural gas producer companies.

8 Holley, C.E., Jr., Vanderzee, Cecil and Westrum, E.F., Jr., Bull. Chem. Therm. 21, p 476-479, 1978.

9 For example, the use of the two laws of thermodynamics leads to the Clapeyron equation which relates the volume change in a phase change and the slope of the phase boundary in a P-T plot (both, in essence, mechanical properties) to the heat involved in the phase transition (a thermal quantity). Thus only two of these kinds of data are needed. With the advent of a molecular theory of thermodynamics the relationship between heat and mechanical energy

could be "understood" but such a molecular theory was not necessary for the development of the Clapeyron relationship.

10 Reynolds, W.W., Chem. Eng. Prog. 68, p. 29-35, September 1972, esp. Figure 5.

11 Private communication, plant manager of an ethylene plant.

12 Rudd, D.F. and Watson, C.C., "Strategy of Process Engineering", John Wiley and Sons, Inc., New York, N.Y., 1968, p. 349.

13 ibid, p. 455 where eleven process simulation languages are listed. That list is not exhaustive, however.

14. Hartley, D.L., "Technical Aspects of Efficient Energy Utilization," Summer Study 1974, American Physical Society, New York, N.Y., p. 23. See also Physics Today, Aug. 1975, p. 23-33 and references herein.

15 See reference 1., Introduction p. vii.

16 Baker, O., Proc. 39th Annual Convention Natural Gas Processors Association (1960).

17 Squires, E.W. and Orchard, J.C., Proc. 47th Annual Convention Natural Gas Processors Assoc. p. 80-85, March 19, 1968.

18 Leland, T.W., Chappelear, P.S. and Gamson, B.W., AIChE J. 8, p. 482 (1962).

19 Othmer, D.F., Ind. Eng. Chem., 34 p. 1072 and p. 1504 (1942).

20 Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., "The Properties of Gases and Liquids, "McGraw-Hill, New York, N.Y., 1977.

21 Zudkevitch, D., Hydrocarbon Processing, March, 1975, p. 97-103.

22 ibid

23 This is in the process of being rectified through a project supported by a combination of the U.S. Government and an industrial consortium. For information, contact Dr. Howard White, Office of Standard Reference Data, National Bureau of Standards, Washington, DC 20234.

24 Private communication.

25 Albright, M.A., Proc. 49th Annual Convention-Natural Gas Processors Assoc. p. 14-20, March 17, 1970.

26 Cryogenics and Industrial Gases, p. 9-13, Sept/Oct. 1973.

27 See, for example, Hirshfelder, J.O., Curtiss, C.F., and Bird, R.B., "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York N.Y., 1954.

Present and Future Sources of Fluid Property Data

Fluid Property calculations for the design and operation of large process systems require that the data used by the engineer be in a computer compatible form. This, in turn, places complex demands on those of us in the data generation and correlation field. The responsibility of the producers of data, i.e., experimentalists, theorists or correlators, to the ultimate users of the data such as design engineers is discussed, because the efficient transfer of data from the originator to the ultimate user is absolutely essential. The specific requirements for data in the future will be for 'black box' type computer-compatible routines to calculate broad ranges of thermophysical properties for pure fluids and mixtures. Although calculational packages are very useful tools, reliance on them by the uninformed can lead to costly design errors and there is some evidence that the existence of the packages may tend to reduce future research in fluid properties. Generic solutions to the future data requirements of the chemical process and energy industries will place heavy reliance on theoretical approaches. Illustrations of the future data requirements of specific industries are given as examples.

N.A. Olien
Thermophysical Properties Division,
National Engineering Laboratory,
National Bureau of Standards,
Boulder, Colo.

ABSTRACT

Fluid Property calculations for the design and operation of large process systems require that the data used by the engineer be in a computer compatible form. This in turn places complex demands on those of us in the data generation and correlation field. The responsibility of the producers of data, i.e., experimentalists, theorists or correlators, to the ultimate users of the data such as design engineers is discussed, because the efficient transfer of data from the originator to the ultimate user is absolutely essential.

The specific requirements for data in the future will be for 'black box' type computer-compatible routines to calculate broad ranges of thermophysical properties for pure fluids and mixtures. Although calculational packages are very useful tools, reliance on them by the uninformed can lead to costly design errors and there is some evidence that the existence of the packages may tend to reduce future research in fluid properties. Generic solutions to the future data requirements of the chemical process and energy industries will place heavy reliance on theoretical approaches. Illustrations of the future data requirements of specific industries are given as examples.

INTRODUCTION

We have witnessed an increasing emphasis on more sophisticated forms of fluid property data over the past several decades. One large factor in this emphasis was the emergence of the aerospace industry and the many requirements imposed by NASA, some of which were described in the previous paper (1). The modern computer, of course, was another major factor, but NASA and its stringent demands for very high accuracy and reliability truly set us on a path from looking up discrete values in handbooks to representing a continuum of properties with computer programs. One of the pioneering efforts in this was the refinement of the Benedict-Webb-Rubin equation of state by Strobridge (2), an effort which was only possible because of the modern digital computer. Calculations, as such, however, are not new. James Conant, the former president of Harvard tells a story, perhaps apocryphal, that took place during World War I (3). When President Wilson appointed a board, with Thomas Edison as chairman, to give scientific advice to the Navy during the course of the war, one of the members chosen by Edison was a physicist from the National Bureau of Standards. Edison told the President that the reason for the presence of the physicist was, "we might have one mathematical fellow in case we have to calculate something out." I am not sure whether the story is appropriate or not in this centenary of Edison's greatest invention (4). Some things have changed since 1918. The direction we are taking in mathematical modeling and the concurrent rapid increase in speed and storage capacity of computers means that the changes will come at an even faster rate. The advent of the microprocessor and other offspring of large scale integration serve to magnify this trend. Those of us producing data must be prepared to be active participants in the introduction of our data and the form of our data into industrial automation. We must work with current and emerging industries to see that they have the best data and formulations available for their use. It is not enough to make excellent measurements, develop magnificent equations of state and the like. I can say from experience that the probability of use of data, models, etc. in industry approaches zero as the estoric nature of the data and models increases. To put it bluntly, if data are difficult to find or hard to use they just will not be utilized. The automation trend mentioned previously serves only to strengthen this tendency. I say this despite the large economic incentives of using more accurate data.

ECONOMIC IMPACT AND LEVERAGE

There have been several studies and estimates made of the economic impact on selected industries of inaccuracies in fluid property data (5,6,7,8,9). One such study is included in this meeting of the ASME. (10). David Zudketvitch has done a great deal in this field and has recently shown (11) that the capital and operating costs of several types of plants can be significantly reduced as a result of increased accuracy (reliability and reduced error bands) of thermophysical property data. Table 1 shows the relative importance of several kinds of data on the design of various parts of process plants. The information in this table is taken from the pioneering work of Zudkevitch (12). It is readily apparent that phase equilibria data are the most vital. This is because the equipment (heat exchangers, distillation columns, compressors, etc.) associated with fluid separation processes is the most capital and energy intensive part of process plants. The large number of liquid-vapor equilibrium correlation techniques gives further credence to the industrial importance of this class of thermodynamic properties. It is reasonably well established, then, that the accuracy of the thermophysical property data of fluids can have a significant economic impact on the industries in which these fluids are used. Let us now look at the magnitude of this potential economic impact.

The chemical process and fuels industries have current annual capital requirements in excess of $50 billion, with the bulk of this in conventional processes and feedstocks. The period 1979–2000 however is a period of transition for these industries with a change to unconventional base feedstocks (principally coal). As an example the American Gas Association has estimated the capital requirements for coal gasification/synthetic gas (SNG) for the period 1978–2000 to be $62.9 billion (see table 2). Liquefied natural gas (LNG) requirements will also be substantial with $7.9 billion for import terminal construction alone in the period 1978–1990. If we add to this the capital requirements for associated distribution and storage systems and dedicated auxiliary plants (e.g., air separation plants for coal gasification and LNG peak shaving facilities) we have projected total requirements in the period 1978–1990 of $83.6 billion and in the period 1991–2000 of $91.5 billion. This $175.1 billion in capital investment will be for process plants and associated equipment involving fluid mixtures ranging from six to eight component LNG to 20 plus component mixtures in coal gas plants. If we remember that this is for supplemental gas for the gaseous fuel industry we can get some idea of the magnitude of the projected capital costs for the total of industries involving mixtures. The potential savings in new plant construction and modification of existing plant as a result of the availability of more accurate data and models is of

Table 1.

RELATIVE IMPORTANCE OF SOME THERMODYNAMIC VARIABLES ON DESIGN AND PERFORMANCE – EVALUATION OF BASIC PETROCHEMICAL PROCESS EQUIPMENT

	VAPOR PRESSURE AND:						RATE DATA	
	DENSITY P-V-T	CRITICALS	PHASE DISTRIBUTION	ELECTROLYTE IONIZATION	ΔH And C_p	ΔS	TRANSPORT	REACTION
REACTORS	C	D	B	S	B	B	B	A
FRACTIONATORS	B	B	A	A	B	D	B	S
EXTRACTORS	B	D	A	D or S	C	D	B	S
HEAT EXCHANGERS	C	B	A	S	A	C	B	S
COMPRESSORS & EXPANDERS	A	A	A	...	A	B	D	S
METERING (AND SALES)	A	...	B	...	S	...	...	....
MATERIALS OF CONSTRUCTION	B	...	B	A	...	...	...	S
POLLUTION ABATEMENT	...	...	A	A	C	...	A	A

KEY:
A – Most important
B – Very important
C – Influences calculations, but accuracy not critical
D – Considered only in preliminary selection
N – Not applicable
S – Important in specific cases

Table 2. Capital Requirements - Supplemental Gas for U.S.
(Billions of 1977 Dollars)

	1978-1990	1991-2000	Total
Coal Gasification/SNG	20.4	42.5	62.9
LNG Importation	7.9	2.0	9.9
Transmission, etc.	55.3	47.0	102.3
Total	83.6	91.5	175.1

Source: Anderson, R., AGA Monthly 60, 30-3 (Apr 1978).

the order of tens of millions of dollars per year. The studies mentioned above also tell us that the savings in operating costs over the life of the plant can be even greater than the savings in capital costs.

EXISTING TABLES OF FLUID PROPERTY DATA

Although there is a strong trend today toward the use of computerized models for calculating fluid property data, tables of property data are still widely used. Table 3 lists some of the more useful of the existing collections which include data on many fluids. You will note that there is a lack of uniformity in the sources of these publications.

Table 3. Collections of Fluid Property Data

LNG MATERIALS AND FLUIDS - A USER'S MANUAL OF PROPERTY DATA IN GRAPHIC FORMAT, D. B. Mann, Editor, National Bureau of Standards, Thermophysical Properties Division, Boulder, CO 80303 (1977) (Supplement 1 - 1978; Supplement 2 - 1979)

THERMOPHYSICAL PROPERTIES OF MATTER/THE TPRC DATA SERIES, Y. S. Touloukian and C. Y. Ho, Editors, Plenum Press, N.Y.

SELECTED VALUES OF PROPERTIES OF HYDROCARBONS AND RELATED COMPOUNDS, Thermodynamics Research Center, Texas A&M Univ., College Station, TX 77843 (also a companion volume on other chemical compounds)

GAS ENCYCLOPAEDIA, L'Air Liquide, Division Scientifique, Elsevier/NorthHolland, Inc. (1976)

ENGINEERING DATA BOOK, Gas Processors Assn., Tulsa, OK (1972)

ASHRAE THERMODYNAMIC PROPERTIES OF REFRIGERANTS, Amer. Soc. of Heating, Refrigerating and Air Conditioning Engrs., 345 East 47th St., N.Y. 10017 (1969)

THERMODYNAMIC PROPERTIES AND REDUCED CORRELATIONS FOR GASES, L. N. Canjar and F. S. Manning, Gulf Publishing Co. (1967)

PHYSICAL PROPERTIES - A GUIDE TO THE PHYSICAL, THERMODYNAMIC AND TRANSPORT PROPERTIES OF INDUSTRIALLY IMPORTANT CHEMICAL COMPOUNDS, C. L. Yaws, McGraw-Hill (1977)

MATHESON GAS DATA BOOK, W. Braker and A. L. Mossman, Matheson Gas Products, East Ratherford, N.J. (1971)

They have been prepared by societies, government agencies, private firms and universities. There are also a number of sets of standard reference data or at least quasi-standard data for equilibrium properties for individual fluids (see table 4). You will notice that some of these are in the process of being revised or at least new versions are definitely planned. The argon and carbon monoxide publications are in great need of revision, but to my knowledge, no definite correlations or critical evaluations are underway. In the case of argon, we have a fluid of relatively small industrial importance, but argon is used so much as a standard for predictions as well as for testing new apparatus that its importance cannot be overemphasized. The state-of-the-art in equations of state has increased significantly since the publication of the Argon Standard Reference Data (13) by the NBS-Office of Standard Reference Data. In addition, a large number of new measurements have been made. The other fluid needing a new correlation is carbon monoxide. I recently completed an informal survey on CO and found to my surprise, that the best wide range tables (14,15) are nearly a quarter of a century old. Another set of tables (16), of slightly newer vintage, does exist, but is limited to the temperature region below 300 K.

METHODS OF CALCULATING FLUID PROPERTY DATA

Many of the references given in table 4 include calculational methods (equations of state). Table 5 lists some calculational methods, the broadest of which is the recently revised Reid, Prausnitz and Sherwood (17). A number of computer calculation packages are available on time-sharing networks for a user fee or for outright purchase. There is even a computer package available in the Soviet Union called AVESTA as illustrated in figure 1. AVESTA stands for Automatic Variable Engineering System of Thermophysical Advance. There are dangers in using computerized calculation packages, since the user can derive a false sense of security about the accuracy of the data returned. The danger is amplified when the data are used directly in computer calculations for plant design and operation. In the latter case the engineer never sees the data and he or she does not have a chance to apply good engineering judgement to the fluid property data. Often higher level managers in technical firms develop a feeling that the calculation packages provide data which have very small or non-existent error bars. This is both disquieting and dangerous. I have heard of a vice-president in the LNG industry who stated that they did not need any more work on LNG phase equilibria, because his company subscribed to a computer package which provided all of that. To illustrate the folly of such a pronouncement, let us examine figure 2. Elliott, et al. (18) made a comparison of K-value calculations from ten different

Table 4. Standard Data for Individual Fluids

Fluid		Source
H_2		McCarty, R. D., NASA SP-3089 (1975)
He		McCarty, R. D., J. Phys. Chem. Ref. Data 2, 923 (1973)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 4, Butterworths (1977)
N_2 *		Jacobsen, R. T. and Stewart, R. B., J. Phys. Chem. Ref. Data 2, 757 (1973)
O_2		Roder, H. M. and Weber, L. A., NASA SP-3071 (1972)
F_2		Prydz, R. and Straty, G. C., NBS Tech. Note 392 Rev. (1973)
Ar		Gosman, A. L., McCarty, R. D., et al., NSRDS-NBS 27 (1969)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 1, Pergamon (1971)
CO		Din, F., Thermodynamic Functions of Gases, Vol. I, Butterworths (1956)
CO_2		Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 3, Pergamon (1976)
NH_3		Haar, L. and Gallagher, J. S., J. Phys. Chem. Ref. Data 7, 635 (1978)
CH_4		Goodwin, R. D., NBS Tech. Note 653 (1974)
	and	Angus, S., et al., Intern. Thermodynamic Tables of the Fluid State - 5, Pergamon (1978)
C_2H_6		Goodwin, R. D., et al., NBS Tech. Note 684 (1976)
C_3H_8 *		Goodwin, R. D., NBSIR 77-860 (1977)
$n\text{-}C_4H_{10}$		Goodwin, R. D., NBSIR 79- (1979)
$i\text{-}C_4H_{10}$		Goodwin, R. D., NBSIR 79- (1979)
C_2H_4 *		Angus, S., et al., Intern. Thermodynamic Tables of the fluid State - 2, Butterworths (1974)
C_3H_6 *		Juza, J., et al., Acta Tech. (Prague) 23, 425 (1978)

*Newer versions underway or planned.

Table 5. Calculation and Estimation Techniques

THE PROPERTIES OF GASES AND LIQUIDS, Third Edition, Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., McGraw-Hill (1977)

PHYSICAL PROPERTIES - A GUIDE TO THE PHYSICAL, THERMODYNAMIC AND TRANSPORT PROPERTIES OF INDUSTRIALLY IMPORTANT CHEMICAL COMPOUNDS, C. L. Yaws, McGraw-Hill (1977)

A NEW TWO-CONSTANT EQUATION OF STATE, D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam. 15, 59 (1976)(For a review of this and other phase equilibria models, see Renon, H., Fluid Phase Equilibria 2, 101 (1978)

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COMPUTER CALCULATION SYSTEMS, some examples are: CHEMTRAN/CHEMSHARE, CHESS, GPA CONV, SSI, FLOWTRAN, PDA, PPDS, TAP, etc.

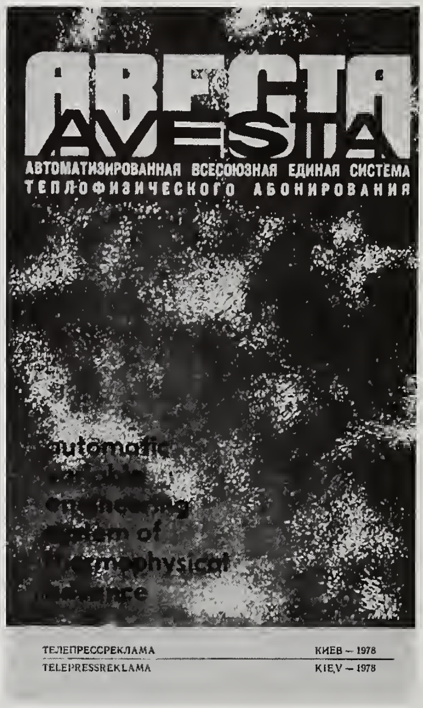

Figure 1. AVESTA-Automated Property Calculation Package from the USSR.

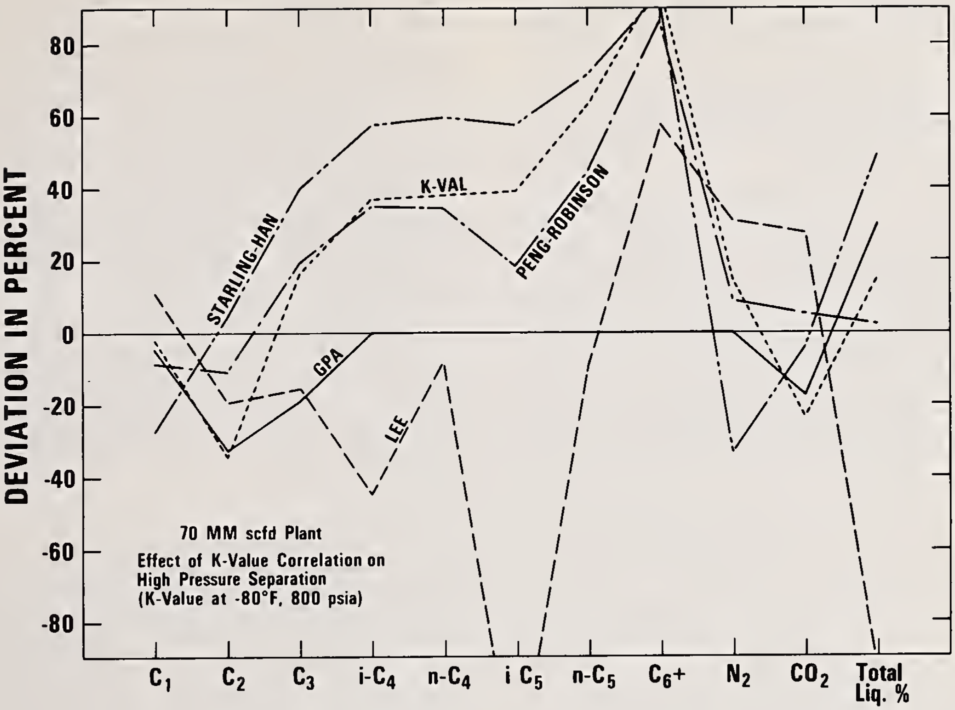

Figure 2. Comparison of K-Value Calculation Methods for Natural Gas.

computer packages. K-values are very useful in designing separation plants and are defined as K = y_i/x_i where: y_i = molar concentration of the i^{th} component in the vapor phase and x_i = molar concentration of the i^{th} component in the liquid phase.

In figure 2 I have shown the deviation of five of these methods from a sixth, arbitrarily chosen. The horizontal axis gives the molecular species (C_1=methane, C_2=ethane, etc.), and the last item is the total volume of all liquids condensed. I think it would be very difficult to maintain that any of those methods represents scientific truth. In fact, the methods examined by Elliott and presented here represent three different approaches to K-value predicting - i.e., conformal solution theory, van der Waals' techniques and empirical methods. One further disadvantage of the widespread availability of these packages was hinted at above. In a conversation with Professor Kobayashi of Rice University a few months ago, he and I agreed that the computer packages tend to stifle research. The attitude expressed by the vice-president mentioned above certainly does not encourage grants and contracts for needed research work. If it sounds as if I am advocating the elimination of calculation techniques, especially computerized methods, let me assure you that this is not the case.

DISSEMINATION OF FLUID PROPERTY DATA IN THE FUTURE

I firmly believe that computerized calculation methods for fluid properties, especially mixture properties, will become commonplace in the future. First, automation in design requires automation in data; second, data needs are so great as to demand the use of semi-automated calculations; and third, in the case of mixtures, tables are just not practical. How can we do this and still avoid the disadvantages described above? It is essential that calculational packages be accompanied by well documented and justified confidence limits, the existence and use of which is clearly understood by the users of the packages. In addition, the package should contain provisions for notifying the user when calculations are requested which are outside the range of the particular method used. What is needed is a 'truth in packaging' requirement for calculational techniques. A little earlier, I said that producers of data (experimenters, theorists or correlators) must be prepared to participate in the introduction of their data and models into industry. They must also do their part to prevent their data from being misused, i.e., unwarranted extrapolations. The objective should be wide-range and accurate models, which can be easily used and which, if they do not prevent improper use, at least clearly provide warnings of perils ahead. One of the blessings of the modern computer is the ease with which we can provide for warnings of this sort.

Often the engineer is either faced with a need for professional advice about calculational methods and data or is at a loss as to where to turn. In these cases, it is important to make a personal contact with knowledgable experts in fluid properties. Table 6 lists several 'Data' or 'Information Analysis Centers' which can be of great assistance to the engineer.

Table 6. Fluid Property Data Centers

Chemical Kinetics Information Center
NBS - Robert F. Hampson, (301) 921-1000, extension 2565

Chemical Propulsion Information Agency
Johns Hopkins, (301) 953-7100

Chemical Thermodynamics Data Center
NBS - Donald D. Wayman, (301) 921-1000, extension 2773

Cryogenic Data Center
NBS - Neil A. Olien, (303) 499-1000, extension 3257

Electrolyte Data Center
NBS - Bert R. Staples, (301) 921-1000, extension 3632

Thermodynamics Research Center
Texas A&M - R. C. Wilhoit, (713) 846-8765

Thermophysical Properties Research Center
Purdue - W. H. Shafer, (800) 428-7675

EXPANDED NBS PROGRAM IN FLUID PROPERTY RESEARCH

The Thermophysical Properties Division at NBS-Boulder has embarked on a long range effort to develop generic techniques for predicting the thermophysical properties of a broad range of industrial fluids. We are building on the experience we have gained through our participation in programs in liquefied natural gas (LNG) (primarily funded by the American Gas Association and the Gas Research Institute) and ethylene properties (a joint government-industry program, managed by the NBS-Office of Standard Reference Data). Our work has established a rational approach to the development of accurate and useful mathematical models. This approach involves the judicious marriage of experimental measurements, theoretical studies, mathematical modeling and a continuing interaction with current and future users of the models and data. The measurement aspect of this integrated program will occupy a substantial fraction of the available resources, but even at that we realize that the plan will be measurement limited. The measurements will be primarily on pure components and binary systems, with a strong need for very careful choice in fluids and measurement ranges. In addition the measurements must be of high quality, as the literature is replete with examples of measurements of little or no use because of the high uncertainty of the results. A purely experimental approach to mixtures properties rapidly leads to an infinite data requirement; therefore, theoretically based models must play a large role in the entire project. It is difficult to separate the theoretical efforts from the mathematical modeling work. We are conducting and have plans to accelerate our experiments wherein fluids are modeled in a computer by the techniques of molecular dynamics (19). These methods have the potential of becoming very powerful tools in the quest for a basic understanding of fluid behavior and the development of soundly based methods of predicting the properties of complex fluid mixtures. One area which requires a large amount of attention is the need for quantitative understanding of the interactions between unlike molecules. Included in this are molecules of disparate sizes (e.g., molecular mass ratios of 25 or greater) and even more complex interactions (e.g., polar-nonpolar interactions.)

All of this cannot be accomplished by one group in Boulder and we thus plan to continue a large number of very productive technical collaborations. Two of these are with the Thermophysics Division and the Office of Standard Reference Data, both located in the National Measurement Laboratory of NBS-Gaithersburg.

CONCLUSION

Even the person on the street is aware of the pervasiveness of the computer in all aspects of modern life, industrial and otherwise. This trend, will continue and people producing fluid property data and models must consider this trend in consideration of the future. These computerized mathematical models must be developed with a combination of intelligence and pragmatism. We must have a clear picture of our engineering customers and their requirements. They in turn must understand what they are getting from us and how best to use the tools we provide.

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The Influence of Thermophysical Properties on the Design and Sizing of Geothermal Power Plant Components

H. E. Khalifa
United Technologies Research Center,
East Hartford, Conn.

J. Kestin
Brown University,
Providence, R.I.

The paper presents a study of the influence of uncertainties in the thermophysical properties of the working fluids on the preliminary design and sizing of the major components of a power plant. The effect of these uncertainties is discussed first qualitatively to characterize the nature of the problems resulting from them, then quantitatively to determine the relative magnitude of the differences in component design and size that would result if a power plant is designed on the basis of different sets of working fluid properties. Special emphasis is placed on isobutane which appears to be attractive for geothermal energy extraction.

ABSTRACT

The paper presents a study of the influence of uncertainties in the thermophysical properties of the working fluids on the preliminary design and sizing of the major components of a power plant. The effect of these uncertainties is discussed first qualitatively to characterize the nature of the problems resulting from them, then quantitatively to determine the relative magnitude of the differences in component design and size that would result if a power plant is designed on the basis of different sets of working fluid properties. Special emphasis is placed on isobutane which appears to be attractive for geothermal energy extraction. A preliminary evaluation of four equations of state for isobutane was conducted to determine the important sizing parameters of the primary heat exchanger and the working fluid turbine for a supercritical Rankine cycle. It is shown that the presence of a pinch point in the heat exchanger plays a major role in magnifying the effect of the differences between the equations. These differences appear to be significant enough to alter the conclusions of optimization studies of geothermal power plants of the binary-fluid type.

INTRODUCTION

In low temperature power cycles, such as those employed in geothermal power generation and waste energy recovery systems, large quantities of heat must be transferred first from the primary source of energy to the working fluid, then from the working fluid to the cooling medium after the work-producing process. Energy conversion systems operating at low heat addition temperatures are, therefore, burdened by a large capital investment associated with large, expensive heat exchangers. The economic optimization of the design of these systems requires a careful balance between the thermodynamic advantage of minimizing the entropy production in the system and the initial cost saving resulting from a cheaper, less efficient system.

In order properly to address the question of system optimization, the designer must have access to reliable sources of the thermophysical properties of the working fluids. These properties affect the design on two levels. On the first level, the equilibrium properties of the working fluids are needed to define the initial and final conditions for the processes constituting the thermodynamic cycle. On the second level, both the equilibrium and transport properties are needed for the detailed design of the system components, including fluid flow mechanics and heat and mass transfer.

In this paper we evaluate the effect of the working fluids on the design of geothermal power plant main components - the heat exchangers and the turbines. A qualitative assessment of the potential effect of these uncertainties is given at first. An evaluation of the uncertainties in the prediction of the thermodynamic properties of isobutane is used subsequently to exemplify the magnitude of the resulting effects on the surface area of the primary heat exchanger and the characteristic dimensions of the turbine in a binary-fluid geothermal power plant.

Nature of the Problem

The production of work from low-temperature energy sources poses difficulties that are not normally encountered with high-temperature sources. The main difficulty resides in our inability economically to manufacture efficient expanders that would utilize a low-grade thermal energy source directly. Thus, practical energy conversion systems for low-grade energy sources must comprise a process through which a vapor working fluid is generated, then subsequently expanded in a conventional turbine to produce useful work. Among the most attractive of these practical systems is the so-called binary-fluid system shown schematically in Fig. 1-A. The binary-fluid system is based on the simple Rankine cycle whose temperature-enthalpy representation is shown in Fig. 1-B. Systems of this kind have been proposed and/or built for the utilization of geothermal energy, solar energy, waste energy, ocean thermal energy, etc., with a wide selection of working fluids for each case.

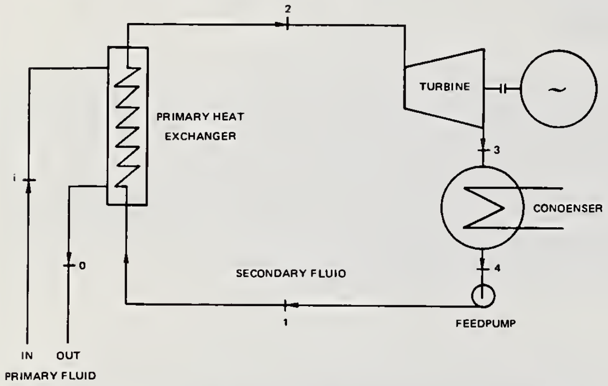

Figure 1-A. A flow diagram of a binary-fluid power plant.

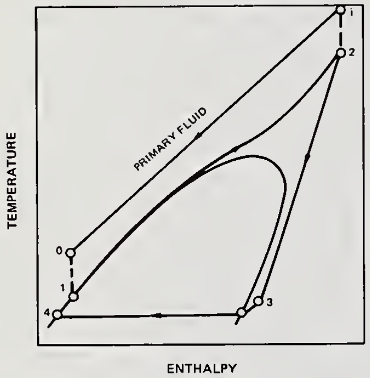

Figure 1-B. A temperature-enthalpy representation of a supercritical binary-fluid cycle.

The selection of the optimum working fluid for any given application is a fundamental task in the design of binary-fluid energy conversion systems. Of the large number of candidate working fluids for a given application, many can be excluded on the basis of such factors as chemical stability in the desired temperature range, toxicity, explosiveness, etc. The remaining ones must be screened according both to thermodynamic and to economic considerations. For each fluid, preliminary performance and design data must be obtained over a range of cycle parameters to determine the optimum conditions. Considering the necessity of repeated access to the thermophysical properties of the working fluids over the whole domain of operating conditions, and the sheer magnitude of the effort involved, the use of a computer becomes indispensible. Even so, it is often the case that the developers of computer optimization codes would opt for inaccurate, but simple, representations of the thermophysical properties of the working fluids for the sake of reducing the computation time. Such a compromise would be acceptable if the results of the optimization studies are quoted with their associated uncertainty or if the optimum is insensitive to the errors introduced by the inaccurate representation of the properties. Unfortunately, this is not always the case.

In the primary heat exchanger of a binary system, for example, the temperature profile exhibits a pronounced pinch as illustrated in Fig. 2. Also depicted in Fig. 2 are the temperature profiles as would be obtained from alternative representations of the thermodynamic properties of the working fluid. It is not uncommon to design these heat exchangers with a pinch point temperature difference of 5°C, particularly in low temperature energy conversion systems where the available temperature difference between the source and the sink is low. The impact of temperature differences of the type shown in Fig. 2 on the surface area requirements in the primary heat exchanger can be substantial as will be shown later.

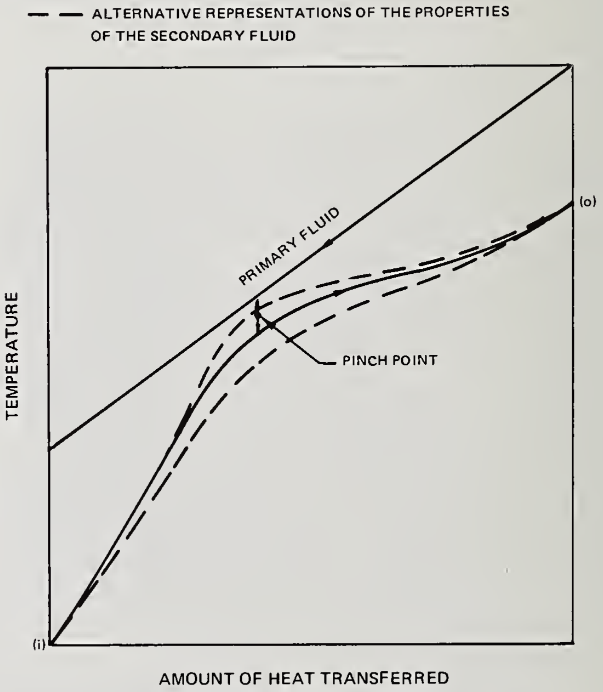

Figure 2. Temperature distribution in the primary heat exchanger.

The problems resulting from the uncertainties in the properties of the working fluids are further compounded by the fact that low-temperature power cycles often operate in, or close to the critical region. Additional uncertainties are, therefore, introduced because the simple correlations used for optimization studies are invariably analytic in the critical region and thus fail fundamentally to describe the anomalous critical behavior. The effect of this uncertainty may be reduced somewhat if refined analytic equations, such as that of Keenan, Keyes et al. for steam, are developed for the large number of the organic working fluids advocated for low temperature power cycles.

Thermophysical Properties for Design

The most common representation of the equilibrium thermodynamic properties of a working fluid is a combination of a PVT equation and the ideal-gas properties of the fluid which, together, formulate the fundamental equation for the fluid. Among the most widely used PVT equations are the Benedict-Webb-Rubin (BWR) equation for hydrocarbons (1,2,3) and the Martin-Hou (MH) equation for fluorocarbons (2,4,5), or variations on these. Starling has correlated the properties of a large number of light petroleum fluids and a number of fluorocarbons by means of a modified Benedict-Webb-Rubin equation (MBWR) (3,6). Optimum parameters for the Martin-Hou equation as applied to a number of geothermal binary cycle working fluids can be found in Ref. (7). Both equations, augmented by an appropriate expression for the specific heat in the ideal-gas limit, have been extensively used for geothermal binary cycle optimization. It should be mentioned, however, that in most cases, the equation parameters were derived from a limited set of experimental data, the accuracy of many of which was not reliably established.

Reliable data on the transport properties of many of the working fluids are noticeably lacking. This situation is partially mitigated by the fact that transport properties affect the design indirectly through averaged parameters such as the friction factor, the overall heat transfer coefficient, the drag coefficient, etc. These parameters tend to depend only weakly on the transport properties of the working fluid in many practical situations. It has been argued, therefore, that transport properties need not be known to the same degree of accuracy as equilibrium properties for preliminary screening and design optimization studies. Nonetheless, reliable data would be needed for the final design of critical components.

Equilibrium Properties of Isobutane

Isobutane has been identified as one of the primary candidates to be used as the working fluid in geothermal binary power plants (7,8,9). In fact, geothermal pilot and demonstration plants, using isobutane as a working fluid, have been either designed or built both in this country and abroad (10).

An extensive survey and compilation of the equilibrium and transport properties of isobutane was conducted by Kestin, et al (11). Several formulations of the PVT properties of isobutane were identified, notably:

[1] A modified Benedict-Webb-Rubin (MBWR-1) equation developed by Starling (3).
[2] A refinement of the above equation (MBWR-2) developed later by Starling et al. (6).
[3] A differential-regional BWR equation (DRBWR) developed by Eubank et al. (12).
[4] A revised Martin-Hou equation (RMH) developed by Milora et al. (5).

In each case, the PVT equation was supplemented by an expression for the ideal gas enthalpy or isobaric specific heat to complete the fundamental formulation of the equilibrium properties.

The four equations were subjected to a critical intercomparison as well as to comparison with raw experimental results to characterize the nature of the differences among the four equations and between each equation and the experimental data (13).

The four equations provide smooth representations of the properties over a wide range of conditions extending from the ideal gas limit to several times the critical density. Equation [4], however, results in intersecting isotherms in the high density region at supercritical pressures. The use of equation [4] without modifications in this region is, therefore, not recommended. Starling's two equations [1] and [2] represent thermodynamically consistent formulations of the equilibrium properties of isobutane. Aside from the ideal gas properties, which were taken from API project 44 (14), equations [1] and [2] do not require any supplementary correlations. The vapor pressure is obtained by equating the fugacity of the vapor and liquid phases and the latent heats are guaranteed to satisfy the Clausius-Clapeyron equation. In contrast, formulations [3] and [4] are supplemented by correlations for the vapor-pressure and for the saturated liquid density. Consequently, thermodynamic consistency is not built in these formulations.

Reference (13) contains an extensive comparison between each of the four formulations and raw experimental data. The results are summarized in Tables 1-4 for the following sets of experimental PVT data:

(i) Data of Sage and Lacey (15) in the temperature range 21-121°C in both the vapor and liquid regions.
(ii) Data of Beattie et al. (16) for the supercritical temperature range 150-300°C.
(iii) Data of Beattie et al. (17) in the critical region.
(iv) Data of Morris, Sage and Lacey (18) in the temperature range 38-238°C for pressures up to 35 MPa in both the vapor and liquid regions.

The deviations in the liquid region are large as a consequence of the steepness of the P-V isotherms in this region and do not necessarily indicate failure of the equations in this region.

Table 1

Sage and Lacey Data (15)

$[(P_{calc}-P_{ex})/P_{ex}] \times 100\%$

Temp (°C)	Eqn.	Subcritical Density	Supercritical Density
21.11	[1]	-0.19% to +0.28%	+4.5% max
	[2]	-0.1% to +4.7%	too large
	[3]	-1.01% max	too large
	[4]	-0.4% max	too large
71.11	[1]	+2.1% max	-13% to +6%
	[2]	+2.5% max	+9% max
	[3]	+0.25% max	+36% to +6%
	[4]	+1.3% max	too large
121.11	[1]	+2.4% max	-13% to +29%
	[2]	+2.6% max	-10% to +3%
	[3]	+1.3% max	-2% to +3.5%
	[4]	+1.7% max	-12.5% to 14%

Table 2

Sage and Lacey Data (16)

$[(P_{calc}-P_{ex})/P_{ex}] \times 100\%$

Temp (°C)	Eqn.	Subcritical Density	Supercritical Density
150	[1]	-0.14% to +0.24%	-8.3% to +12.8%
	[2]	-0.52% to +0.25%	-9.4% to +1.4%
	[3]	-0.56% to +0.02%	+0.9% max
	[4]	-0.24% to +0.26%	-1.8% to +2.5%
200	[1]	-0.1% to +2%	-0.3% to +6.9%
	[2]	-0.5% to +0.3%	-5.7% to +1.6%
	[3]	+0.25% max	+1% max
	[4]	+1.3% max	-0.6% to +2.7%
250	[1]	-0.3% to +2.4%	+5.5% max
	[2]	-0.7% to +0.2%	-2.2% to +0.8%
	[3]	+0.3% max	-0.3% to +1%
	[4]	+1.8% max	+2.6% max

Table 3

Selected Data of Beattie et al. (around critical temp)(17)

$[(P_{calc}-P_{ex})/P_{ex}] \times 100\%$

Temp(K)	Eqn.	Subcritical Density	Supercritical Density
407.75	[1]	-0.3% to -1%	-1% to +0.6%
	[2]	-1.5% to +0.2%	-1.8% to -2.8%
	[3]	+0.1% max	-1% max
	[4]	+0.1% max	-0.1% to +0.1%
408.13	[1]	-0.7% to -1%	-0.3% to -1%
	[2]	-0.5% to +1.7%	-1.7% to -2.4%
	[3]	+0.05% max	-0.45% max
	[4]	<0.05%	<0.05%
408.15	[1]	-1% max	-1% to +0.75%
	[2]	-0.2% to +1.6%	-1.6% to -2.6%
	[3]	+0.05% max	-1% max
	[4]	<0.05%	+0.15% max
408.30	[1]	-0.4% to -0.95%	-0.9% to +0.8%
	[2]	-1.6% max	-1.6% to -2.6%
	[3]	-0.5% max	-1% max
	[4]	<0.05%	+0.15% max

Table 4

Morris, Sage and Lacey Data (18)

$[(P_{calc}-P_{ex})/P_{ex}] \times 100\%$

Temp (°C)	Eqn.	Subcritical Density ($\rho < 220$ kg/m^3)	Supercritical Density ($\rho > 220$ kg/m^3)
37.8	[1]	-	< 5%
	[2]	-	-20% (or more)
	[3]	-	-20% (or more)
	[4]	-	excessive
71.1	[1]	-	∿10-20%
	[2]	-	5% max
	[3]	-	+40% to -10%
	[4]	-	excessive
104.4	[1]	-	+25% to -15%
	[2]	-	+5% to +10%
	[3]	-	-10% to +4%
	[4]	-	excessive
137.8	[1]	+0.5% max	+23% to -13%
	[2]	+0.7% max	+7% to -12%
	[3]	-0.7% max	+5% max
	[4]	+0.4% max	+19% max
171.1	[1]	-0.2% to +0.7%	+10% to -11%
	[2]	-0.25% max	+2% to -11%
	[3]	-0.4% to +0.1%	+2% max
	[4]	-0.1% to +0.5%	+3% max
204.4	[1]	+0.5% max	+6% to -10%
	[2]	-0.7% max	+0.7% to -13%
	[3]	+0.4% max	-4% max
	[4]	+0.5% max	+3% max
237.8	[1]	-0.5% to +1%	+5% to -5%
	[2]	-1% max	+0.5% to -9%
	[3]	-0.2% max	-0.7% max
	[4]	+1% max	+0.8 to -1.8%

A detailed analysis of the deviations and their distribution (13) indicates that none of the four equations is decidedly superior to the others. One equation may be a better representation of the experimental data in one region but may be poorer than the other equations in other regions. The distributional disparity of the deviations among the four equations can produce significant differences when these equations are used independently to design a given power plant component or to optimize the design of a whole system.

Effect on System Components

In order to demonstrate the practical importance of the differences that exist among the four correlations, each correlation was used in a number of typical design calculations associated with a Rankine cycle geothermal power plant.

Cycle efficiency. The four correlations were used to calculate the conditions at the four key points in a supercritical Rankine cycle characterized as follows:

- Turbine inlet temperature, T_1 175°C
- Turbine inlet pressure, P_1 7.5 MPa
- Condenser pressure, P_2 (T_2) 0.5 MPa (38°C)

The cycle thermodynamic efficiency was calculated and is listed together with the other properties in Table 5. It can be seen that the cycle efficiency computed from the four correlations are nearly the same and that the differences in the boiler heat input and in the turbine work output are small (about 2 percent). In other words, the differences among the four correlations do not manifest themselves as differences in the cycle efficiency.

Table 5

Comparison of Cycle Parameters

$T_1 = 175°C$, $P_1 = 7.5$ MPa, $P_2 = 0.5$ MPa, ($T_2 \simeq 38°C$)

Eqn.	T_2 (°C)	h_1 (kJ/kg)	h_2 (kJ/kg)	(h_1-h_2) (kJ/kg)
[1]	49.8	428.5	335.9	92.6
[2]	48.6	425.8	334.3	91.5
[3]	47.5	416.6	327.1	89.5
[4]	47.5	420.2	329.8	90.4

Eqn.	h_3 (kJ/kg)	h_4 (kJ/kg)	(h_1-h_4) (kJ/kg)	(h_1-h_2)/(h_1-h_4) (%)
[1]	313.5	-3.9	432	21.4%
[2]	314.3	-1.8	428	21.4%
[3]	308.2	-5.4	422	21.2%
[4]	311.5	-1.8	422	21.4%

Primary heat exchanger. The four equations were used to determine the surface area of a counterflow primary heat exchanger (see Figs. 1, 2), subject to the following conditions:

- The hot fluid (geothermal water) is an imcompressible fluid with a constant specific heat
- No pressure loss in the heat exchanger passages.
- Constant local heat transfer coefficient.

The last assumption is a major simplification since the local heat transfer coefficient in an actual heat exchanger will tend to vary appreciably along the heat exchange surface due to changes in the local fluid properties and due to the variation in the local fouling resistance.

The heat exchanger was divided into one hundred small sections and the surface area was determined by a combination of numerical and graphical techniques for the following specified conditions:

- Water inlet temperature, T_{wi} 200°C
- Isobutane inlet temperature, T_i 35°C
- Water outlet temperature, T_{wo} 50°C
- Pinch temperature difference, ΔT_{pinch} 5 & 10°C

The results of these calculations are summarized in Table 6. The last column of this table shows that for the same water mass flow, the four equations yield heat exchanger areas that differ by as much as 10 percent for a specified pinch temperature difference of 10°C, and by as much as 18 percent for a pinch temperature difference of 5°C. Even for two equations as close as equations [1] and [2], the surface area differs by a significant 8 percent at the lower pinch temperature difference. Typical temperature profiles are shown graphically in Fig. 3 for equations [1], [3] and [4].

Table 6

Results of Calculations for a
Water-Isobutane Counterflow Heat Exchanger

$T_i = 35°C$, $T_{wo} = 50°C$, $T_{wi} = 200°C$

(a) Pinch-point temperature difference = 10°C

Equation	T_o (°C)	$\dot{m}/\dot{m}_w$	$A/\dot{m}_w$ $m^2/(kg/s)$
[1]	143	1.43	331
[2]	143	1.43	339
[3]	153	1.22	351
[4]	138	1.72	318

(b) Pinch-point temperature difference = 5°C

Equation	T_o (°C)	$\dot{m}/\dot{m}_w$	$A/\dot{m}_w$ $m^2/(kg/s)$
[1]	154	1.3	500
[2]	154	1.3	539
[3]	162	1.14	540
[4]	140	1.56	458

Turbine. The specific available work (exergy) at the turbine inlet (emerging from primary heat exchanger) is given by

$$w^o = h_o - h_r - T_r (s_o - s_r) \qquad (1)$$

in which h and s refer to the specific enthalpy and entropy, respectively. The subscript r designates a reference dead state taken here as saturated liquid at 25°C. For a specified power output, $\dot{W}$, the required mass flow is given by

$$\dot{m} = \dot{W}/w^o \qquad (2)$$

The characteristic velocity in the turbine is proportional to the square root of w^o, i.e.,

$$V^* \alpha \, (w^o)^{1/2} \qquad (3)$$

while the characteristic turbine flow area is given by

$$A^* \alpha \, \dot{m}/\rho^* V^*, \qquad (4)$$

in which ρ^* is a characteristic density taken here as the density at the turbine inlet.[1] The turbine

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[1] It is more common to choose the turbine exit density for this purpose.

characteristic dimension can thus be defined

$$\Delta \equiv (\rho^*)^{-1/2} (w^o)^{-3/4} \qquad (5)$$

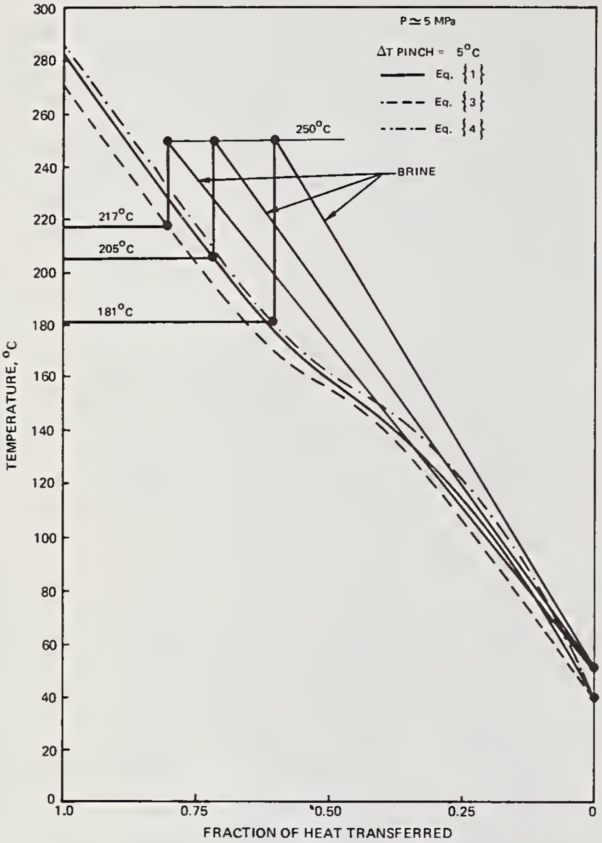

Figure 3. Characteristics of primary heat exchanger.

Table 7 contains a comparison of the turbine characteristic dimension for the four correlations when the specified pinch point temperature difference is 10°C. It can be seen that the turbine characteristic dimension obtained on the basis of different equations varies by as much as 10 percent. This is a direct consequence of the differences in the heat exchanger exit conditions (turbine inlet conditions).

Table 7

Turbine Characteristic Dimension

Equation	Exergy at Turbine Inlet (kJ/kg)	$\Delta \times 10^3$
[1]	95	2.90
[2]	96	2.89
[3]	105	2.98
[4]	86	2.70

Concluding remarks

It has been shown that alternative formulations of the equilibrium properties of a working fluid may yield significantly different values of the key design and sizing parameters for the major components of a geothermal binary-fluid power plant. The origin of these differences resides in the sensitivity of the size of the primary heat exchanger in these plants to the location of the pinch point and to the temperature differences in the vicinity of this point. These effects are more pronounced for lower specified pinch temperature differences. It is thus conceivable that systems optimized on the basis of one formulation could lead to optimum design and sizing parameters that differ from those obtained on the basis of another formulation. It is emphasized that these uncertainties strongly depend on the degree of success of the various correlations in representing experimental data and in incorporating the essential physical features of the fluid behavior over the domain of interest. An accurate representation in the critical domain, for instance, must account for the singular nature of the critical point and for the anomalous behavior of the fluid there (19).

Users of computer design and optimization programs, therefore, must keep in mind that, with the limited accuracy of the experimental data for many of the organic working fluids suggested for binary fluid cycles, it would be unjustified to attach practical significance to differences in cost of the order of 5 or 10 percent, unless, of course, it can be shown that the design is relatively insensitive to the uncertainties in the thermophysical properties.

Once a particular fluid has been identified as the most attractive working fluid for a given application, its properties must be accurately measured, then carefully correlated to provide a standard formulation for subsequent detailed design and performance verification.

Acknowledgments

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Thermophysical Properties of Rocks: A Perspective on Data Needs, Sources and Accuracy

H.P. Stephens

S. Sinnock

Sandia Laboratories,
Albuquerque, N.M.

Recent emphasis on research in geologic isolation of nuclear wastes and geoenergy resource development has created a renewed demand for enginering thermophysical property data of rocks and other geologic materials at elevated pressures and temperatures. In contrast to fabricated engineering materials with specified properties, rocks used in engineering design are complex, naturally occuring materials having properties which must be characterized, rather than specified, for engineering studies. Many difficulties in measuring, reporting, and using thermophysical properties of rocks result from: (a) rock inhomogeneity and anisotropy on both microscopic and macroscopic scales, (b) inclusion of pore fluids such as water, and (c) measurement of laboratory properties under conditions quite different from those of material in situ. Because measurements on in situ materials are scarce, many analyses depend on extrapolated values of uncertain accuracy.

ABSTRACT

Recent emphasis on research in geologic isolation of nuclear wastes and geoenergy resource development has created a renewed demand for engineering thermophysical property data of rocks and other geologic materials at elevated pressures and temperatures. In contrast to fabricated engineering materials with specified properties, rocks used in engineering design are complex, naturally occurring materials having properties which must be characterized, rather than specified, for engineering studies. Many difficulties in measuring, reporting, and using thermophysical properties of rocks result from (a) rock inhomogeneity and anisotropy on both microscopic and macroscopic scales; (b) inclusion of pore fluids such as water; and (c) measurement of laboratory properties under conditions quite different from those of material in situ. Because measurements on in situ materials are scarce, many analyses depend on extrapolated values of uncertain accuracy. A survey of thermophysical property data available for geologic thermal transport studies indicates that caution must be taken to effectively match data abstracted from the literature with project objectives.

INTRODUCTION

Recent emphasis on energy resource development and understanding natural terrestrial thermal processes has stimulated a renewed demand for accurate thermophysical property data of rocks and other geologic materials at elevated temperatures and pressures. The purpose of this paper is to provide a current perspective on data needs, sources, and applications of several thermophysical properties of rocks which are needed for engineering design. This perspective will serve to stimulate discussion related to the theme of this session: "Thermophysical Property Information: What Difference Does it Make?"

Both engineering and scientific endeavors have recently accelerated demand for thermophysical property information. For example, systematic study of terrestrial heat flow began about 15 years ago, despite the historical occurrence of dramatic thermal events such as colcanism. Serious analysis of the response of in situ geologic materials to man-induced thermal fields began even more recently. From an engineering standpoint, a knowledge of thermophysical properties of rocks is necessary to design subsurface structures which will withstand the thermal environments to which they will be subjected.

Deep mines have encountered high geothermal temperatures throughout history. However, improved mining techniques have allowed ever deeper penetrations into the earth's interior with a concommitant increase in demand for thermophysical understanding. More recently, research towards developing energy sources other than fossil fuel has created a need for engineering knowledge of thermophysical data for rocks at significantly elevated temperatures and pressures as well as for heated rock systems subjected to non-steady state thermal flux. Although the experience of the authors is primarily related to those rock properties required for design of an effective heat-dissipating mined repository for heat-producing radioactive wastes, it should be noted that other research activities, such as geothermal reservoir engineering for electrical generation and thermal energy storage, require similar geothermal understanding and contribute to the accelerating demand for lithologic thermophysical data.

Any engineering design program consists of two basic stages: first, defining the environment of the structure and second, determining the response of the materials to the environment. With respect to designs which utilize thermal analysis, a knowledge of thermophysical properties is needed for both stages. The exactness of the design and soundness of the resulting structure are related to data accuracy and the validity of design assumptions. Although adequate data are available for most manufactured structural materials, a general lack of thermophysical property information for geologic engineering purposes can sometimes hinder correct design practice. This lack of information is due to several factors, including traditional reliance on simplicity of design and acceptance of relatively high failure risks. However, increasingly complex design, dramatically rising construction costs, and social and economic demand for very low failure risks with respect to performance and safety have placed added emphasis on the need for accurate thermophysical property data of geologic materials.

In the following sections of this paper, we will discuss the data sources for thermophysical properties of rocks; the characteristics of rocks which affect the determination, accuracy, and reporting of property information; and the status and accuracy of specific thermophysical properties.

DATA SOURCES

The thermophysical properties chosen for discussion in this paper are those that significantly affect conductive heat transfer within the earth's crust: thermal conductivity, thermal diffusivity, specific heat and thermal expansion. Although a significant number of references on thermal radiative properties exist, nearly all radiative properties literature to date is associated with emissivity and reflectance of terrestrial surfaces for remote sensing studies at ambient temperatures and is not considered germane to the topic of this paper.

Two sources of published thermophysical property data are available, namely, individual research papers and data compilations. Because of the great amount of time and effort required to find specific properties of interest if they are scattered throughout a diffuse literature, data compilations are a preferred source. However, there are currently no comprehensive, up-to-date compilations of thermophysical property data available for geologic materials. The last published compilation devoted solely to properties of rocks (1) is now over 13 years old and by today's accelerated demand is woefully out of date. A more recent monograph on geothermics (2) contains several tables of thermophysical properties for rocks, but excludes thermal expansion. The most comprehensive and up-to-date compilation of thermophysical property data for materials, the TPRC series (3), has few entries for rocks, and most of these are conductivity data reported before 1963.

Figure 1 shows a rapid increase in thermophysical property information after 1960, with over half of the total references published between 1965 and 1975. This growth curve emphasizes the need for a current compilation that incorporates post-1965 data. Hence, the geothermal engineer must currently rely on individually published papers as his primary source of up-to-date information. Though the arduous task of searching for data is facilitated by a number of computerized bibliographic search and abstract services, there, nonetheless, remains an urgent need for readily available, up-to-date compilations.

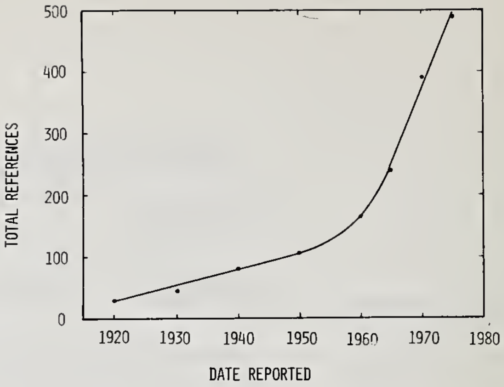

Figure 1. Time-growth curve for thermophysical property data. (Data from a computerized bibliographical search by the Center for Information and Numerical Data Analysis and Synthesis (CINDAS), Purdue Industrial Research Park, Lafayette, Indiana).

In order to illustrate a cursory perspective of the status of thermophysical property information for rocks, properties reported in the references used to construct Figure 1 were grouped in Figure 2 according to properties referenced, major rock category for which the properties were determined, and possible technological category of usage for the data. Several general sets of observations emerge from these histograms.

First, thermal conductivity and diffusivity data comprise half of all thermophysical property information available, while little information (13% of the total) is available for thermal expansion. About one-quarter of the references concern radiative measurements, which are of limited use for thermal analyses of subsurface conditions at elevated temperatures. These radiative properties, as noted above, are primarily associated with remote sensing applications. The small percentage of data on the specific heat of rocks reflects a dependence on calculations from data on individual minerals, rather than laboratory measurements on the mineralogical assemblages of real rocks.

Second, more thermophysical property studies have been made on igneous and sedimentary rocks, including coal, than on metamorphic. It is difficult to speculate about the reasons for this sampling distribution, except to note that metamorphic rocks account

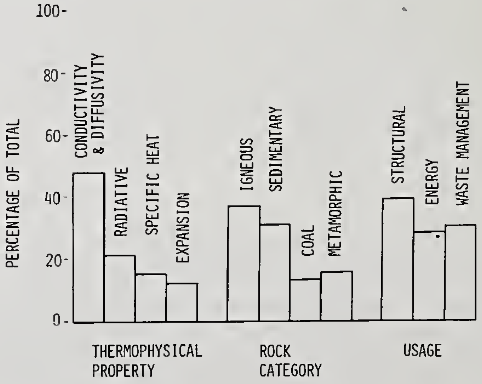

Figure 2. Histograms of thermophysical property data.

for only about 5% of the continental surface areas, whereas sedimentary rocks account for about 75%, and igneous rocks about 20%.

Third, it appears that there are more property determinations on rock types for structural use than those for energy and nuclear waste management use. However, the need for thermophysical property data for energy and nuclear waste technology is growing, and proportionally more data associated with these fields are expected to become available in the future.

PHYSICAL CHARACTERISTICS OF ROCKS

In contrast to manufactured engineering materials with properties which can be specified, rocks are complex, naturally occurring materials having properties which must be characterized, rather than specified. A problem of utilizing published thermophysical property data of rocks in engineering design arises from the classification and characterization of rocks for which the properties are reported. From an engineer's perspective, a rock type is a set of lithospheric materials that behave similarly when subjected to the same or similar environments. However, a geologist considers a rock type to be a visually recognizable and classifiable set of lithospheric materials which may have widely differing material properties. The two objectives for classification do not necessarily coincide. The geologist has created classes of rocks (igneous, sedimentary and metamorphic) based on what he can infer or observe, such as origin and texture, and the class names have been accepted throughout the technical community as a communication tool. Because thermophysical properties depend on physical characteristics which usually cannot be quantified by visual inspection in the field or by microscopic observation, the geologic classification is of limited use for defining thermophysical properties. The fact that rocks are complex materials makes the complete characterization of their physical state difficult, time consuming, and expensive. This has led many investigators to rely only on the simpler method of describing the materials on which thermophysical property measurements were made; that is, the geologic formation name and the location from which the rock was taken. Thus, tabulations of thermophysical property data are commonly grouped by geologic rock classification which results in wide ranges of properties for each rock type. What is needed are tabulations with respect to physical characteristics of the rocks which affect thermophysical properties.

The physical factors which affect the thermophysical properties of rocks can be broadly grouped into two categories: composition and structure. Because rocks are complex aggregates of minerals and other substances, composition and structure must be considered in terms of heterogeneity, fluid inclusions, voids and environmental conditions such as temperature and pressure. Additionally, because engineering analyses may be applied on scales ranging from millimeters to kilometers, all compositional and structural effects must be considered in terms of the scale of interest. If the units are very small (millimeters to centimeters) variation among the mineralogical constituents of a rock are the element of heterogeneity of concern. At successively larger scales, bedding, foliation, microfractures, porosity, vugs, joints, compositional and textural gradients, and finally structural discontinuities dominate the heterogeneity of rock bodies (Figure 3).

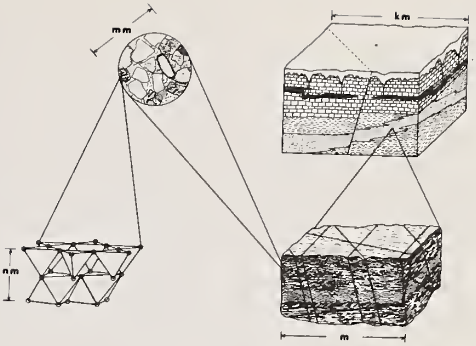

Figure 3. An illustration of the effect of scale on various chemical and physical characteristics of rocks. Lower left: Mineral lattice anisotropy. Upper left: Microsection - mineral phases, cleavage, microfractures, and fluid inclusions. Lower right: Hand specimen - bedding, foliation, porosity, voids, vugs and joints. Upper right: Block diagram - facies changes, veins, fractures, faults, folds, caverns, and watertable.

For many users the assignment of discrete thermophysical properties to geometrically discrete units of rock is required. Scale must again be considered because anisotropy as well as heterogeneity of thermophysical properties is associated with the structure and composition of rock bodies (Figure 3). On the microscopic scale, anisotropy may be due to differences in orientation of mineral lattice, while on macroscopic scales compositional variations due to bedding and foliation planes may reasonably be expected to impart a degree of anisotropy to the properties. Structurally, fracture planes may concentrate along certain directions lending a structural element to anisotropy.

Other significant factors which affect rock properties are fluid content and environmental conditions, i.e., pressure and temperature. The total fluid content, whether hydrocarbon or water, is a function of porosity and may affect thermophysical properties to a degree which can be dominant. The dependence of in situ thermophysical properties upon both temperature and pressure may also be an important consideration since both increase with depth in the earth's crust.

THERMOPHYSICAL PROPERTIES OF ROCKS: STATUS AND ACCURACY

Before presenting a brief discussion of the status and accuracy of specific heat, thermal conductivity and expansion data for rocks, additional caution concerning the use of published data for modeling thermal processes in actual lithologic units is needed. Since in situ field measurements are expensive and difficult, most thermophysical properties of rocks are determined by laboratory measurements. The condition of laboratory samples and the environment under which the measurements are made may vary considerably from the in situ rock body from which the sample was taken. Additionally, laboratory determinations are subject to sampling errors because of the heterogeneity of rock bodies and the size constraints placed on the specimen. Thus, laboratory measurements may not accurately represent properties of rocks in situ.

The most significant advance in thermophysical property measurement techniques over the past several decades has been in measurement speed, not accuracy. The time required for laboratory measurement of many properties has been reduced from hours to minutes as a result of advances in instrumentation and high-speed data acquisition techniques. However, the accuracy of current measurement capabilities has remained about the same. This is undoubtedly due to the fact that the range in reported values for a single rock is dominated more by sample-to-sample variation than instrument error. Another factor which may contribute to experimental inaccuracies is a lack of appropriate standard reference materials for instrumental calibration. Many calibration measurements rely on well-characterized materials such as alumina and quartz which have properties that only approximate those of the rocks to be measured. Because of the variability of even "homogeneous", intact rocks, the development of an accepted "rock" standard material is not likely.

Specific Heat

Even though there are relatively few data on the specific heat of rocks, reasonably accurate values may be obtained from data published for minerals for several reasons. First, there is little variation in the specific heat for different rock types at constant temperature. At room temperature, for example, the specific heat of almost all types of dry rock is 0.20 ± 0.03 cal/g K.[1] Second, the variation with temperature of the specific heat of minerals is well characterized, and the variation with respect to lithospheric pressures of engineering concern is insignificant. Third, the specific heat of rock at fixed temperatures depends only on composition. Because there are tabulations (3-7) of the specific heat of most minerals and oxides as a function of temperature, the specific heat of rocks may be calculated, if the composition is known, by summing the contribution of each constituent phase at the desired temperature:

$$C_p = \sum_i x_i C_{p_i} \qquad (1)$$

where x_i = the weight fraction and C_{p_i} = the specific heat of the i^{th} constituent.

Specific heat measurements on rock samples may be made by drop calorimetry, adiabatic calorimetry, and several dynamic comparative techniques such as differential scanning calorimetry. Depending on the type of apparatus and temperature range, the instrumental accuracy of these techniques ranges from a fraction of a percent to several percent. Most routine determinations for rocks have an accuracy of 2 to 10 percent. Because the specific heat of most rock-forming minerals is known to comparable or better accuracy (4), the heat capacities of rocks can be calculated, according to equation (1) to an accuracy of better than 10%. Table 1 illustrates the above points by comparing experimental values (8,9) for the specific heat of four rocks with the values calculated by equation (1). The calculated values are close to or within the range of the reported (8,9) experimental values.

In the use of mineralogical data for calculating the specific heat of rocks, several other factors such as water content, phase changes and chemical decomposition reactions must be considered. Water can contribute significantly to the specific heat of rock, and its heat of vaporization can give rise to a large thermal effect. Temperature related phase changes are common for many minerals and care must be taken to use the appropriate specific heat. One must also be careful not to extrapolate specific heat equations for minerals beyond the temperature of chemical decomposition.

Thermal Conductivity and Diffusivity

Unlike specific heat which depends only on composition, thermal conductivity and its related quantity, thermal diffusivity, depend on both the composition and structural condition of the rock. The thermal conductivity k is derived from the equation for the heat flux $\vec{q}$ which for the one-dimensional case is given by

$$q_x = -k \frac{dT}{dx} \qquad (2)$$

where dT/dx is the temperature gradient. The thermal diffusivity α, which determines the rate of heat propagation in transient thermal processes, is defined in terms of the conductivity, specific heat C_p and density ρ:

$$\alpha = \frac{k}{\rho C_p} \qquad (3)$$

Both k and α can be determined experimentally.

As pointed out above, about half the literature on thermophysical properties for rocks concerns thermal conductivity and diffusivity. It is beyond the scope of this paper to review the extent of this literature in detail. However, it is worthwhile to note that recent investigations are devoted to unraveling the complexities of the effects of rock composition and structural condition upon thermal conductivity. Among the characteristics and parameters studied are cracks and porosity (10-14), chemical and mineral composition (15-17), moisture and fluid content (18-20), anisotropy (21-22), and temperature and pressure (9,23-27).

Until this decade, most conductivity data were reported by rock type. This led to wide ranges in values for each category reported (Figure 4). Only recently have investigators started correlating physical and chemical characteristics of rocks with conductivity (17,28,29).

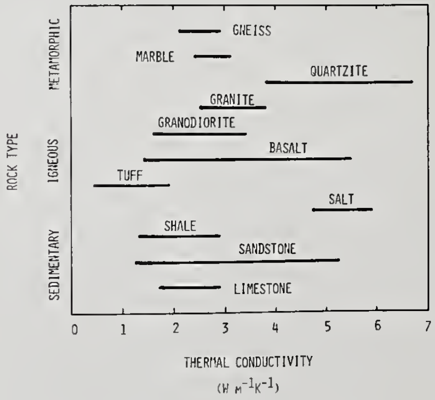

Figure 4. The range in thermal conductivity date reported for various rock types.

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[1] 1.0 cal/g K = 4.184 kJ/kg K in SI units.

TABLE 1

Comparison of Experimental and Calculated
Specific Heat for Several Rocks

Rock Type	Source	Petrographic Mineral	Analysis Vol. %	Temp (K)	Specific Heat Exp (Ref 8)	($cal\ g^{-1}\ K^{-1}$) Exp (Ref 9)	Calc
Sioux Quartzite	Jasper, MN	Quartz	99+	300	‡	0.174	0.178[a]
				380	0.219	0.201	0.209
				500	0.243	0.231	0.237
				800	0.303	‡	0.267
Holston Marble	Knoxville, TN	Calcite	99	300	‡	0.198	0.197[b]
		Magnetite & purite	< 1	380	0.237	0.220	0.227
				500	0.254	0.246	0.251
				800	0.292	‡	0.282
Rockville Quartz Monzonite	Rockville, MN	Microcline	34	373	0.222	‡	0.210[c]
		Plagioclase	29	800	0.278	‡	0.271
		Quartz	30				
		Biotite	6				
		Hornblend & apatite	< 1				
Dresser Basalt	Dresser, WI	Plagioclase	50	300	‡	0.186	0.176[d]
		Pyroxene	45	380	0.231	0.209	0.205
		Magnetite	5	500	0.246	0.234	0.230
				800	0.283	‡	0.261

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‡ - beyond experimental range or not reported. a - calculation based on quartz. b - calculation based on calcite. c - calculation based on maximum microcline, albite, quartz, and phlogopite. d - calculation based on anorthite, diopside, and magnetite. Data for calculations from reference 4.

Brief descriptions of current laboratory techniques for thermal conductivity and diffusivity measurements are found in several recent publications (2,29,30). Although the inaccuracy of most instruments is within several percent, uncharacterized sample conditions may cause measurement imprecisions of 10 to 20% in experiments which are otherwise carefully controlled. Under some circumstances the experimental error may be much greater. For example, it has recently been reported (20,31) that errors up to 100% may result when the conductivity of porous rocks saturated with low conductivity fluids is measured. Metamorphic rocks have been found to exhibit conductivity anisotropies of 20 to 50% (22). Additionally, the conductivity of low porosity, dry rock measured in the laboratory can be a factor of two (18) lower than the conductivity in situ, where the rock may be saturated with water and lithostatic pressure can close cracks. Thus, before thermal conductivity data are used, their source must be carefully evaluated to ensure that the accuracy matches the required need.

Thermal Expansion

The thermal expansion of rocks, like thermal conductivity, depends on both rock composition and structural condition. The term "thermal expansion" may refer to either the coefficient of linear expansion or volumetric expansion. The coefficient of linear expansion ε represents the change in length ΔL of a unit length L resulting from a temperature change ΔT of one degree:

$$\varepsilon = \frac{1}{L}\frac{\Delta L}{\Delta T} \qquad (4)$$

For materials which have isotropic expansion characteristics, the volumetric expansion coefficient β is given by

$$\beta = 3\varepsilon \qquad (5)$$

However, most rocks expand anisotropically and therefore β must be derived from their volumetric dilation or from measurement of ε in several directions.

As shown in Figure 2, data for thermal expansion of rocks are sparse, and only within the last several years have studies been initiated to determine the influence of the composition and structural condition on expansion. Several investigations have shown that thermal expansion of rock at ambient pressure depends on the constituent minerals (32), porosity (33), the presence and development of microcracks within the rock (33-35), and dehydration of glasses and minerals (33). For an unconfined sample, the presence of microcracks leads to a smaller value of the thermal expansion coefficient than that predicted from the constituent minerals. However, development of microcracks in a sample during measurement significantly increases the expansion coefficient. Dehydration can be responsible for a net contraction at temperatures where the dehydration occurs. Because extent of cracking and dehydration depends on heating rate, laboratory determinations of thermal expansion at different heating rates may show wide variations for the same rock sample. Hysteresis may also be evident when multiple measurements are made during heating and cooling cycles. As an example of errors which may be encountered, one investigator (33) reports 10-15% variations for laboratory expansion measurements on different samples of the same rock specimen.

The effect of lithostatic pressure on the thermal expansion of rocks is largely unevaluated. It has been calculated from compressibility data that a lithostatic load of 100 MPa reduces the thermal expansion coefficient of porous rocks as much as 25% (26). Determinations (36) at pressures up to 400 MPa indicate that above a rock dependent critical pressure between 50 and 200 MPa, thermal expansion approaches the value calculated for the mineral aggragates. Because the lower range of these critical pressures is close to those encountered in environments for deep geologic isolation of nuclear waste, it is important to quantify this effect.

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Thermophysical Property Data: Who Needs Them?

R. C. Hendricks
NASA Lewis Research Center,
Cleveland, Ohio

Specific examples are cited herein to illustrate the universal needs and demands for thermophysical property data. Applications of the principle of similarity in fluid mechanics and heat transfer and extensions of the principle to fluid mixtures are discussed. It becomes quite clear that no matter how eloquent theories or experiments in fluid mechanics or heat transfer are, the results of their application can be no more accurate than the thermophysical properties required to transform these theories into practice, or in the case of an experiment, to reduce the data. Present-day projects take place on such a scale that the need for international standards and mutual cooperation is evident.

ABSTRACT

Specific examples are cited herein to illustrate the universal needs and demands for thermophysical property data. Applications of the principle of similarity in fluid mechanics and heat transfer and extensions of the principle to fluid mixtures are discussed. It becomes quite clear that no matter how eloquent theories or experiments in fluid mechanics or heat transfer are, the results of their application can be no more accurate than the thermophysical properties required to transform these theories into practice, or in the case of an experiment, to reduce the data. Present day projects take place on such a scale that the need for international standards and mutual cooperation is evident.

NOMENCLATURE

Roman

D = diffusion coefficient
F_λ = scale function for thermal conductivity
F_η = scale function for viscosity
f = scale function of fluid α relative a reference fluid
G = Gibbs free energy
G_R = reduced mass flow rate, $G_R = \rho u/G^*$
G^* = mass flow normalizing parameter, $G^* = \sqrt{P_c \rho_c / Z_c}$
h = scale function of fluid α relative a reference fluid
m = molecular weight
P = pressure
$P_R = P/P_c$ = reduced pressure
R = gas constant
T = temperature
$T_R = T/T_c$ = reduced temperature
u = velocity
v = specific volume
x = mole fraction
$Z = PV/RT$ = compressibility factor

Greek

η = viscosity
θ = shape factor
λ = thermal conductivity
μ = symmetric function
ν = asymmetric function
$\xi_{\alpha\beta}$ = binary interaction parameter
ρ = density
ϕ = elementary asymmetric function
Φ = shape factor
$\phi_{\alpha\beta}$ = binary interaction parameter

Subscripts

c = critical
m = mixture
o = reference fluid
α = computed fluid
α,β = binary interaction
$\alpha\alpha,\beta\beta$ = pure component interaction

INTRODUCTION

Who needs thermophysical property data? Ask any company manager with a deadline to meet and no way to proceed until thermophysical properties data become available. When this happens, management will permit its engineers to go to extremes to acquire the needed information quickly. The number of times this occurs makes it clear that data, or methods for their prediction, are needed on the shelf in anticipation of need.

Furthermore, present day applications take place on such a scale with materials and energy so costly that it is no longer acceptable to simply use "just any old properties" to describe a fluid, but rather more faithful reproduction of the fluid properties at the desired conditions is now required.

The need for accurate, consistent, universally acceptable thermophysical property data and representative computer programs are requirements of industry, government and universities alike throughout the world in advance of specific applications.

In a treatise on thermodynamics, Zeleznik (1) wrote that thermodynamics perhaps more than any other physical theory pervades the fabric of physical science; as a corollary, I would suggest that thermophysical properties which heuristically relate the physical nature of matter, pervade our daily lives. Applied and basic disciplines alike in such areas as engineering, medicine, physics, chemistry, biology, to cite only a few, rely heavily on adequate thermophysical property bases. Yet thermophysical property data usually arouse little interest or concern on the part of the engineers and management until such information is needed and found to be unavailable; an even more detrimental situation arises when management thinks that the data are available, but the information - which has not been critically evaluated - is wrong. Somehow it is always assumed that such properties either will be available or predictable when needed. Due to this prevailing philosophy many of the advances in thermophysical property measurements, techniques of representation and computer programs for rapid production of this information are developed in response to an urgent request. The aerospace industry found a need for new property data sets with nearly every major project and more recently a similar need has arisen in the natural gas industry. On some rare occasions, and through the diligent efforts of a very few, new property sets have been available when required. Organizations as NBS, CODATA, NASA, IUPAC at Imperial College, TPRC at Purdue, AGA in conjunction with the AIChE, the ASME and the Electric Power Utility Industry have sponsored such programs.

How can engineers and scientists benefit from systematic studies of accurate thermophysical property information? Subsequent sections will discuss some project needs related to the development of data bases using para-hydrogen as an example of a well defined program and data set, and RP1 (JP etc.) as examples of sets where more efforts are required. Furthermore, we shall cite a few property related projects in the area of fluid mechanics using property similarity principles and in the area of metallic, ceramic and plastic materials. Finally, we shall look into the Van der Waals' one-fluid model to relate thermodynamic and transport properties of some one-component and multicomponent fluids and indicate directions toward generalization of the application of corresponding states.

SOME DEVELOPMENTS IN THERMOPHYSICAL PROPERTIES INSTIGATED BY THE AEROSPACE INDUSTRY

The following section will illustrate some projects and related development of one of the world's finest data bases using para-hydrogen as a specific example, and indicate some current activities including multicomponent mixtures and RP (kerosene).

Some Developments Related to Para-Hydrogen

Even before this country had a space program, mission analysis codes clearly demonstrated the advantages of propellants with high specific impulse. From the combustion analysis program of Huff, Gordon and Morrell (2) H_2-O_2 and H_2-F_2 were identified as two of the most promising propellant combinations. Early literature searches for properties of H_2 (3), O_2 (4) and F_2 (5) revealed a dearth of information and the need for thermophysical property data for these fluids became urgent.

With hydrogen designated as the engine coolant and NACA transformed into NASA, a substantial effort was launched in collaboration with the National Bureau of Standards at Boulder to determine the properties of hydrogen, oxygen and fluorine. We will look specifically at the development of the hydrogen data base where the classic work of Woolley, Scott and Brickwedde (6) was our initial guide but whose limitations had become transparent.

One of the early problems we faced was the long term storage of liquified hydrogen. Over 75% of the liquified hydrogen just vanished after a few days, clearly an intolerable situation for any space mission. While the tank insulations were poor, they were not that poor. We discovered that at ambient temperatures hydrogen wasn't really hydrogen at all, but a mixture of 75% ortho and 25% para hydrogen. Further, the equilibrium composition varied with temperature, with substantial property changes, notably in enthalpy, specific heat and thermal conductivity; it turned out that at 20K hydrogen consists of 99% parahydrogen as illustrated in fig. 1 and 2. Thus the ortho-hydrogen would simply boil off leaving the smaller quantity of para-hydrogen. Ortho-para conversion units were researched and installed (7) and long term storage of hydrogen became a reality, but only after the additional development over a period of years of the thermophysical properties of insulations and superinsulations (see fig. 3).

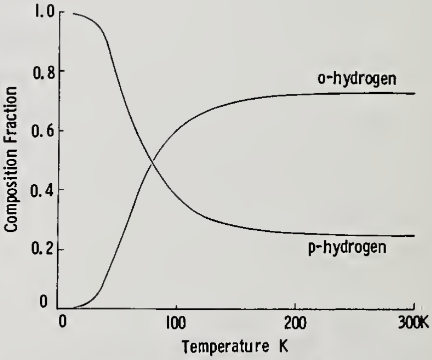


Figure 1. - Composition dependence of hydrogen.

Concurrent with the thermophysical properties work at NBS-Boulder, heat transfer and fluid dynamics studies were undertaken, with results that appeared completely contradictory to known theories and expermental results. For example, in fully developed turbulent flows, the wall temperature increases in a monotone manner over the length of the heated tube. However, with hydrogen, the profile increased to a maximum followed by a monotone rise. (9, 10, 11) (see fig. 4). As a consequence, the need for thermophysical property data of para-hydrogen and for understanding catalytic conversion became even more acute.

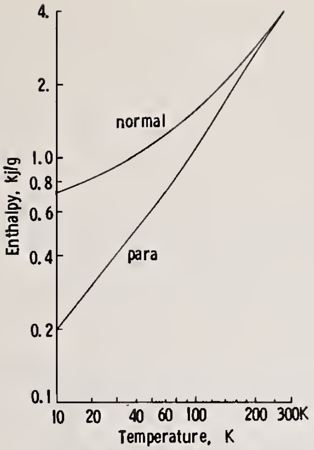


Figure 2a. - Enthalpy of normal and para hyrogen at one atmosphere.

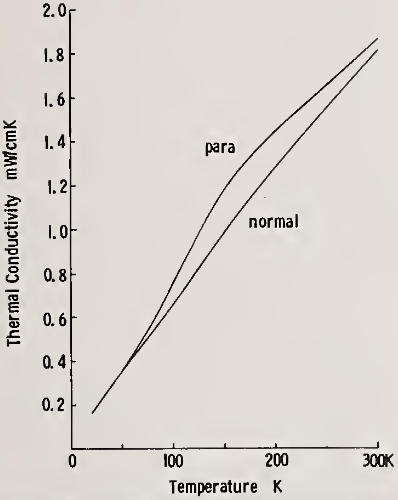
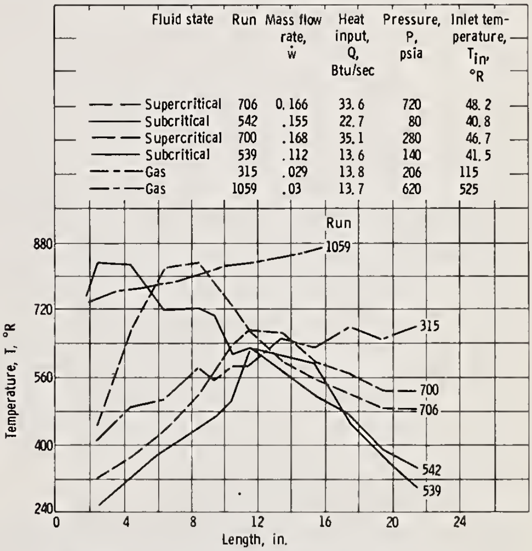


Figure 2b. - Thermal Conductivity of Gaseous Hydrogen at One Atmosphere.

Figure 3. High efficiency insulation (MLI).

Goodwin's data compilation (12) and Goodwin's simplified equation of state (13) along with a computer program developed by Harry (14) and generalized property charts of Thodos et al. (15,16) proved adequate to resolve a few of the early heat transfer and fluid dynamics problems. But, as in any field where accurate, consistent property data are lacking, we found different researchers, manufacturers and people from the nuclear industry in disagreement as to which computer codes and properties to use. On many occasions we would sit around a table, peek at our computer output and ask, "What number did you get?" as if there existed some magical set of proprietary properties to explain the differences in the calculated results for that particular application. Recognizing this problem, NASA launched an early effort toward unification. For example, early computer codes by Roder (17) and Farmer (18) though fast, lacked uniformity, and suffered from the lack of adequate quantitative data.



Fluid state	Run	Mass flow rate, $\dot{w}$	Heat input, Q, Btu/sec	Pressure, P, psia	Inlet temperature, T_{in}, °R
Supercritical	706	0.166	33.6	720	48.2
Subcritical	542	.155	22.7	80	40.8
Supercritical	700	.168	35.1	280	46.7
Subcritical	539	.112	13.6	140	41.5
Gas	315	.029	13.8	206	115
Gas	1059	.03	13.7	620	525

Figure 4. - Surface temperature distribution with axial position for near-critical and gaseous hydrogen. Tube inside diameter, 0.335 inch.

With the classical data of Goodwin (19) and the extension of the BWR (Benedict-Webb-Rubin) equation of state proposed by Strobridge and Stewart (20), Roder and Goodwin (21) produced the first accurate representation of the PVT surface for para-hydrogen at temperatures up to 300K. With this equation of state, based on accurate, consistent and extensive data and the measurement of transport properties by Diller and Roder, the entire industry began to settle down. Experimental heat transfer and fluid dynamics results could now be placed in proper perspective even though many could not yet be correlated and experimentalists and engineers stopped trying to assess the impact of differences between poor properties and the fact that our understanding of the dynamics of the application was totally inadequate (24).

The loss of many man-years of effort, duplication and unnecessary proof of concept projects could perhaps have been avoided if adequate thermophysical property information had been available when needed. Since that time, the Lewis Research Center of NASA has supported an ongoing effort at NBS and an effort at the University of Maryland to minimize the recurrance of such events; to date we have been moderately successful in assessing the state of the art in the areas of high pressures, fluid mixtures, transport properties and thermophysical properties in the critical region of fluids. We have not yet been successful in the attempt at unification, but it is an area which must be confronted and overcome both on a local and international scale. I might add that the hydrogen and oxygen data bases represent the most extensive, accurate and consistent sets in existence.

Current efforts are toward exploring a) the thermophysical properties of hydrogen and oxygen to 100 MPa (≃15000 psia) for future mission applications, and b) the basic concepts needed for predicting the thermophysical properties of fluid mixtures, and c) the nature of thermal conductivity and viscosity including their anomalous behavior near the critical point.

Why are we still interested in property data? It is obvious that high pressure applications will increase payload and decrease the costs while the spinoffs to landbased power systems appear substantial in terms of increased efficiency. As for mixtures, if we could determine how to predict the PVTx properties of a simple mixture of an organic-inorganic fluid, with substantially different critical points and vapor pressure curves, from the extensive yet smaller data sets associated with the pure components, we could project a generalized method for predicting the PVTx surface of any simple mixture. The near critical region provides a key to understanding thermophysical property surfaces, and while thermodynamics of the critical region have received much attention, the transport properties have not. Sengers et al. (25) have been able to assess the anomalous thermal conductivity in the critical region for a number of fluids. The anomalous thermal conductivity is strong and can be related to the divergence of compressibility. Recently Basu and Sengers have also proposed an equation to account for a very weak anomaly in the viscosity of fluids near the critical point (26). Efforts in these areas are making remarkable advances.

Some developments related to RP1

Concurrent with the effort to develop high performance propellants, a large effort was launched to improve the propellant kerosene or RP1 as it was designated. In this case, a sound systematic program as completed for hydrogen, was not undertaken and unfortunately I must report that thus far little has been added to our fundamental understanding. Neither a uniform PVT computer code or data base for these fluids is available covering high pressures and the transport properties are of questionable value. The effort could benefit from a mixtures program and pure component hydrocarbon data bases. Even though the data base is of questionable value, we are currently seeking to understand the effects of coking both in the fluid and combustion gas states.

Theoretically, early RP rocket engines were not cooled adequately to prevent burnout of the coolant passages. A careful inspection revealed that a thin layer of coke formed on the thruster side of the coolant passage which protected it against the extreme temperatures and thermal fluxes. Coking has been studied by petrol producers, (27,28,29) and was found to be quite sensitive to oxygen and sulfur compounds in the fuel. These compounds also markedly changed the reported heated tube data (30) where coking was found. No systematic effort has been undertaken to determine the nature or limitations of coking in coolant passages (thermostability) even though hydrocarbons are the mainstay of our transportation industry in the form of fuels and lubricants. The problem is compounded when shale derived fuels are considered.

We should assess the availability of data for RP, incorporating results of the mixtures and pure component data base programs, and provide the industry with a representation of the PVT and transport properties data to 100 MPa (≃15000 psia). We should then investigate the limits of heat transfer to 80MW/m^2 (≃50Btu/in^{2}sec) with wall temperatures to perhaps as high as 2000K.

While these examples serve to illustrate the developments related to aerospace, the results have been extensively used by industry in general. Data bases for oxygen (31), fluorine (32), FLOX (33), nitrogen (34), helium (35) and selected hydrocarbons (36,37,38) have been established for NASA by NBS-Boulder.

Some Other Property Bases and Related Applications

In this section, we cite some other data bases of interest to NASA and industry. Some organizations where such data can be found are covered in the papers of Olien and Liley presented at this meeting.

NASA has had projects concerned with the thermophysical properties of systems other than fluids with the purpose of establishing data bases for superconductors, slushes and gels, combustion, and such materials as metals, refractories and plastics. We will only briefly mention some of these.

In the area of superconducting magnet technology and low temperature physics NASA has produced several magnets, developments in magnet wire and coatings such as formvar. Currently there is some interest in MHD.

In the area of ultra high pressures and transition points, the potential of an ambient temperature superconductor initiated a study on the possibility of compressing hydrogen to the metallic state which may require a pressure of 4 Mbars. Many semiconductor to metal transitions have also been studied (39,40). More recently the production of metallic neon has been achieved (41). A spinoff of this work is the gadolinium heat pump which has the potential of achieving near Carnot efficiency (42,43,44).

Free radical fuels offer very high impulse potentials and have stimulated work in producing atomic hydrogen propellant; however, free radicals are difficult to stabilize and produce and little effort is currently given to it.

Slush propellants have increased bulk densities, increased coolant capacity and reduced boiloff losses. A slush is readily produced in small quantities through evacuation of the container, but NBS produced p-H_2 slush using a novel refrigeration scheme (45). NBS has also determined the properties of some slushes.

Gels have been considered for thermal stability of fuels and fire inhibitors, and in some cases for providing increased performance (46). The problems with gels and slushes is in transfering them: they tend to clog up pumps and adhere to the containers and for RP mixtures the tendency is toward formation of waxes.

In the area of plastics, the need for high temperature (to 600°F) polymer matrix composites led Serafini (47,48) to develop PMR (in situ polymerization of monomer reactants) polyimides. In the PMR approach, the reinforcing fibers are impregnated with a solution containing a mixture of monomers dissolved in a low boiling point alkyl alcohol solvent. The monomers are essentially unreactive at room temperature, but react in situ at elevated temperatures to form a thermo-oxidatively stable polyimide matrix. These highly processable addition-type polyimides can be processed by either compression or autoclave molding techniques. PMR offers superior processing versatility, high temperature properties and finds application in advanced engine and airframe concepts.

Refractories are used in many engine components where complexity precludes adequate cooling for conventional materials (49). For example, a two-layer system with a bond coating of nickel-chromium-aluminum-yttrium (Ni-16Cr-6Al-.6Y) and a ceramic coating of yttria-stabilized zirconia (ZrO_2-$12Y_2O_3$) has been tested in several applications. Similar refractory coatings are being applied to turbine blades and rubbing surfaces (50,51,52) to reduce gas path sealing losses and increase engine efficiency (53).

Directions toward better property representation

In this section we shall a) discuss the application of the principle of similarity to thermophysical properties and fluid mechanics (i.e., a move toward generalized transforms) and b) suggest a merger of the extended corresponding states concepts with the thermophysical properties function of Zeleznik (54) i.e., a move toward generalized thermophysical property representations.

Toward a Generalized Transform

The strongest impetus toward generalization is the insight gained by comparing experimental results for fluids α and β; the implication that experimental data taken with a cryogen are applicable to, say water, and vice versa, is of significant value.

Based on the engineering needs for properties in heat transfer and fluid flow computations we advocated earlier that simple fluids could be represented accurately, consistently and extensively by a form similar equation, but with different coefficients. Based on Bender's equation for five fluids, (55), we were able to produce a uniform properties computer code GASP for eight fluids (currently twelve) and subsequently the code WASP for water. Armed with these codes and the principle of similarity we began to explore the utility of this approach. It was found that we could

i) extend fluid ranges in PVT and determine the character of the surface derivatives,
ii) produce reduced Joule-Thomson coefficients and the reduced Joule-Thomson locus for many fluids,
iii) produce representations for the anomalous behavior of the thermal conductivity in the critical region for most of these fluids,
iv) correlate two-phase choked flow data and predict these results analytically,
v) group experimental heat transfer results over a relatively wide range of fluid conditions, and
vi) produce a wide variety of normalized property parameters for several fluids which could then be represented in reduced form on a single chart.

Currently order for many of these fluid property related projects and concepts can be found using the work of NBS and Mollerup (57-59), where the properties of two pure substances can be related by the equations[1]

$$Z_m[v,T,x] = Z_o[v/h,T/f]$$

$$G_m[v,T,x] = fG_o[v/h,T/f] + RT(\sum_\alpha x_\alpha \ln x_\alpha - \ln h)$$

where o denotes the reference fluid and the properties are termed configurational, because they have similar molecular potentials, i.e. both are adequately described by two-parameter potentials. For $x = 1$, the equations relate the properties of two pure components while for $x \neq 1$ the relation expresses the properties of a multicomponent mixture. The functions f and h are dependent on the ratio of the critical temperature and volume, and for pure components,

$$f = \left(\frac{T_\alpha{}^c}{T_\alpha{}^c}\right)\theta \qquad h = \left(\frac{v_\alpha{}^c}{v_o{}^c}\right)\Phi$$

the parameters θ and Φ being weakly dependent functions of temperature and volume (60,61).

For mixtures, we need to account for the energy of mixing, introduce some "mixing rules", and redefine f and h as

$$h = \sum_\alpha \sum_\beta x_\alpha x_\beta h_{\alpha\beta} \quad ,$$

$$fh = \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta} h_{\alpha\beta} \quad ,$$

where

$$f_{\alpha\beta} = \xi_{\alpha\beta}(f_{\alpha\alpha} - f_{\beta\beta})^{1/2} \quad ,$$

$$h_{\alpha\beta} = \phi_{\alpha\beta}\left(\frac{h_{\alpha\alpha}{}^{1/3} + h_{\beta\beta}{}^{1/3}}{2}\right)^3 \quad ,$$

and where $\xi_{\alpha\beta}$ and $\phi_{\alpha\beta}$ are the binary interaction parameters.

Hanley et al. (62,63) applied these configuration functions and proposed that thermal conductivity and viscosity of mixtures could be related in a similar manner. For pure components

$$\lambda[\rho,T] = \lambda_o[\rho h,T/F]F_\lambda \quad ,$$

$$\eta[\rho,T] = \eta_o[\rho h,T/f]F_\eta \quad ,$$

$$F_\eta = \left(\frac{m_o}{m_\alpha} f\right)^{1/2} \Big/ h^{2/3} \quad , \quad F_\eta = \left(\frac{m_\alpha}{m_o}\right) F_\lambda$$

For mixtures, the functions f and h are as defined previously and F_λ, F_η are redefined using the Enskog theory for the transport properties.

The use of configurational functions f and h, along with an accurate reference equation of state, greatly enhances the users capability to accurately relate thermophysical properties. Its greatest utility comes when a dearth of information exists for pure component α, or a multicomponent mixture, and in gaining mechanistic insights when analyzing the data from transport processes with different fluids or mixtures. However, it does have the disadvantage of being more complex. It requires a very accurate pure component representation; the molecular potentials must be similar and one needs to determine the configuration factors and, for the case of mixtures, the interaction parameters. While fluid mixtures represent a very difficult problem, some progress is being made. Mollerup has determined some interaction parameters of interest for LNG and has written a computer program to predict properties of a few simple fluid mixtures whose configurational properties are closely associated with methane (the major constituent of LNG).

We have pointed out in a separate paper (56) that the conservation equations can be made coordinate AND fluid invariant, noting that the conservation equations and the transport relations for heat, momentun and diffusion are tensors, and the coefficients of proportionality (λ,η,D) can be transformed nearly independently of the fluid. In support of such a proposal,

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[1] This is the so-called van der Waals or one-fluid model.

several examples of applications were cited, where the data sets for different geometries and fluids could be related through the use of similarity, including (56):

1. Two phase choked flows could be grouped for several geometries and multiple fluids (64-66), free jet flows through tubes with Borda and sharp edge inlets (67,68), circular, square, rectangular and triangular inlet geometries (69), and for choked flows of gases a general relation was developed for tubes, annular and tapered convergent annular flows (70).

2. Heat transfer data for developed turbulent flows through tubes, from several investigators, could be grouped for multiple gases, liquids and near critical fluids using volumetric expansion parameters and a density fluctuations model (71).

3. Application of the generalized transformation to calculating two-phase-choked flows, using the various reference fluids, methane, nitrogen and oxygen, and compared to the experimental data (66) as illustrated in figs. 5 and 6. The theoretical calculations are for the most part in good agreement independent of the working fluid and the reference fluid used to calculate the results.

The point here is that many insights have been gained through analysis of the properties and application of the similarity principle. Even more insights could be gained if a uniform method of representing properties were available.

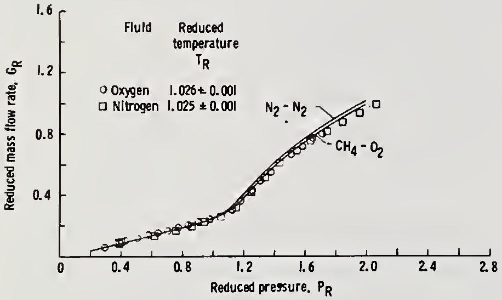

Figure 5. Choked flow rate for reduced temperature of ∿1.025.

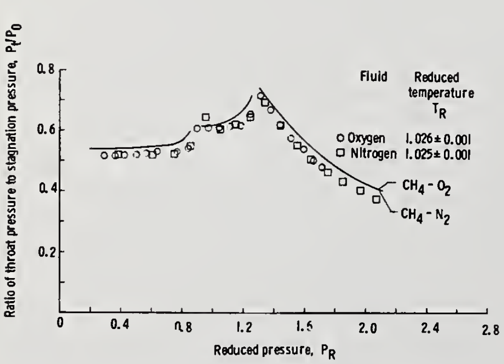

Figure 6. Pressure ratio for reduced temperature of ∿1.025.

Other Thermodynamic Properties Representations

Zeleznik has proposed an elegant linearized relation to represent thermodynamic data which conforms to all the principles of thermodynamics (1,54,72). The relation is

$$G = \sum_{\ell=1}^{N} \phi^{\ell} \sum_{i=1}^{N} \sum_{j=1}^{N} (\mu_{ij}^{\ell} + \nu^{\ell} \ln x_j) x_i x_j$$

where G is the thermodynamic chemical potential, x_i are the mole fractions, ϕ^{ℓ} are the elementary symmetric functions, μ_{ij} the symmetric contributions to G, while $\nu_{ij} \ln x_j$ introduces asymmetry.

In the space considered by Zeleznik, points represent the pure components, edges the binary interactions, and so on to higher order spaces. The theory is quite complex, requiring very large accurate data sets and accurate numerical representation procedures, but the range and potential of this formulation are well documented (72) using data for mixtures as ethanol and n-heptane and ionic solutions such as NaCl + H_2O.

As a logical next step in this approach, it would appear that one should, a) combine the work of Zeleznik, Mollerup and NBS, b) attempt to integrate the principles of fluid similarity, and c) return to mixtures of simple fluids.

In the very restricted framework of fluids whose properties are configurational with methane, we can:

1. usually predict pure component properties which represent end points in Zeleznik's space whether or not such properties in fact exist.

2. often predict properties for binary mixtures which represent the edges or lines joining the points in Zeleznik's space, again whether or not in fact such properties exist.

Once the points and edges of such a space are generated (requiring a lot of computation), one can then use Zeleznik's representation to give properties on and within the surface.

Applying these concepts, the work of Zeleznik (54,72) can probably be extended from a method of representing thermodynamic data to a technique for PREDICTING thermophysical properties. But such a technique would not be as accurate as a formal representation of an extensive data set, is very computational time intensive, and one would probably seek a more simplistic resolution of the problem.

SUMMARY

In summary, we have looked at some problems and development of fluid data bases along with other data bases and some related applications, discussed mechanistic (flow modeling) insights gained from application of the principle of similarity to the conservation and thermophysical property equations; discussed moves toward generalization of thermophysical property representations, and suggested a technique to extend mixture methods.

We have also cited the need for a continuous effort to produce accurate, consistent, extensive thermophysical property data bases which are placed in a form readily accessible to the user and acceptable at the international level.

It should follow that maintainance of an ongoing program in thermophysical properties and international standardization are vital not only to our aerospace and related industrial growth, but our scientific growth as well.

It would seem that too often we operate on the principle that the squeaky wheel gets the grease, but

I think that a well lubricated, properly maintained machine is the most efficient in terms of cost, maintainance, down time, longevity and conservation of basic resources. So who needs properties? - we all do! - and we must continue to support the accurate consistent determination of thermophysical properties.

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Problems and Procedures in Providing Values of Thermophysical Properties of Fluids

P.E. Liley
Senior Researcher, CINDAS,
Professor of Mechanical Engineering,
Purdue University,
West Lafayette, Ind.

For many years, it has been evident that a better knowledge of the thermophysical, i.e., thermodynamic and transport, properties of matter is needed for many technological applications. The present paper gives a brief historical review of some developments made to remedy this situation. This is followed by a survey of correlating equations used for the specific heat at constant pressure, thermal conductivity, viscosity, and Prandtl number of fluids. Finally, recommendations for future work are listed.

ABSTRACT

For many years it has been evident that a better knowledge of the thermophysical, i.e., thermodynamic and transport, properties of matter is needed for many technological applications. The present paper gives a brief historical review of some developments made to remedy this situation. This is followed by a survey of correlating equations used for the specific heat at constant pressure, thermal conductivity, viscosity, and Prandtl number of fluids. Finally, recommendations for future work are listed.

INTRODUCTION

In the middle 1950's some definitive progress in the study of thermophysical properties occurred. This, in part, was produced by war-time technological needs which, for security reasons, only saw a slow declassification and publication. In part, also, they reflected the large expansion in research which occurred then. One item was the publication (1) of "Tables of Thermal Properties of Gases." Originally issued in loose-leaf form (2), these tables represented a large effort and also were possibly the first extensive use of machine (i.e., "computer") generation of thermodynamic functions. At about the same time the "Tables of Thermodynamic Functions of Gases" started to appear. Three volumes were issued (3-5). Each substance was allotted one chapter and different authors were involved. It is unfortunate that consistency in the above of units and bases was not achieved. In large measure, these publications rested on the labors of the late F. Din who made greater use of graphical and approximate methods. The U.K. publications (3-5) concentrated somewhat more on the liquid-vapor boundary, while the U.S. works (1-2) were much preferable at the higher temperatures.

The publications referred to above were followed for several years by a somewhat surprising lack of further material. It is supposed that most persons thought that they fulfilled all needs. But deficiencies became evident in addition to those mentioned above. The study of steam was delegated to a specialist group (6). The almost complete lack of information on transport properties was noted and slowly remedied by the organization of specialist conferences (7) and research programs and publications (8). More detailed studies of thermodynamic properties did result - in the 1960's - and were concentrated in a few centers, such as N.B.S. Boulder, Texas A & M University, etc.

Coupled with the above technological type developments, more scientific type activities appeared. The monumental "Mathematical Theory of Non-Uniform Gases" (9), published in 1939, concentrated on transport properties, and its appearance was soon overshadowed by the World War. Its second edition, in 1952, almost paralleled the separate publication of the "Molecular Theory of Gases and Liquids" in draft (10) and book (11) form. The latter publication also covered thermodynamic properties as well as combustion and quantum chemistry, and thus received wider attention. Its breater use of computer facilities exactly parallels the difference between publications (1) and (3) referred to earlier. The stimulus it gave for engineers to regard a hitherto abstract part of physical chemistry as being useful and usable, which may be exemplified by their summary paper (12), in the opinion of the author, is one of the landmarks of progress in the utilization of thermophysics in this century.

The above efforts must be regarded as being coupled with some other long-term activities. One of these was the American Petroleum Institute Research Project 44, now published with the former Manufacturing Chemists Association tables by the Thermodynamics Research Center (13). In addition to the TRC publications on compounds, an International Data Series on Mixtures has been initiated, and data sheets are currently being issued in two series. Series A covers mixtures of non-electrolytes other than water. Details can be obtained from TRC, College Station, Texas 77843. Series B covers mixtures of organic non-electrolytes in water. Details can be obtained from the Engineering Science Data Unit, 151 Regent Street, London. A further Series D, on metal alloys, is under consideration. Another was the Joint Army, Navy and Air Force JANAF thermochemical tables (14). The cumulative effect of all these efforts was the realization of the need for research centers where studies could be systematically undertaken. These were enlarged and/or established in the late 1950's, as exemplified by the author's own institution (15), the Cryogenic Data Center of the National Bureau of Standards (16), the enlargement of the Mechanical Engineering Research Laboratory[1] (17), etc. The growing awareness of such needs by other countries has led to other institutes being established and international planning and cooperation (18). The material so far presented has aimed at acquainting the reader with a personal, general perspective of historical developments. What follows is a much more detailed account of ways in which four different thermophysical properties have been represented by correlating equations. The four properties were selected due to their importance to heat transfer calculations. In addition, a real lack of knowledge of the transport properties has long been evident in contrast somewhat to the better state of knowledge of the thermodynamic properties. The mission, in part, at the author's center has been to provide values of such properties.

GENERAL APPROACH TO PROPERTY TABULATION

For a particular property and physical state, the literature has to be searched, values extracted, and the entire assemblage of values converted to a given system of units (now S.I.). The property is then plotted as a function of temperature and/or as a function of pressure to detect gross errors or inconsistencies. The selection of the most probable values as reliable input information depends upon several factors. If the values are experimental, the apparatus, method, use, consideration of corrections, etc. are all noted and a comparative ranking of the different sets of data made. If the values are theoretical, the method of calculation is noted, with consideration of any variation in input material, consistency checks, etc. The result of such analysis leads either to a set of experimental data considered reliable, or a set of theoretical values, or both, depending on the input information. In some cases, both sets can show satisfactory agreement with no preference given to either, in which case the average can be taken as input. In other cases, significant differences exist which can be explained and which lead to the selection of either experimental or theoretical values as the more probable basis. In some cases, while significant difference occur, the reasons cannot be explained and a more arbitrary selection must be made, an example based on the securing of agreement in values for chemically similar families of substances.

Whichever case occurs, the selected values are then often represented by a function which is a mathematically convenient, yet physically realistic, representation of the variation of the property. Table 1 lists various representations of thermophysical properties which have been found to be useful where only a temperature dependence is involved. In cases where a simple mathematical function can represent values as well as can a more fundamental function, the simpler function is to be chosen from the viewpoint of user convenience. However, this procedure is not to be adopted in cases where it is feared that the user might be tempted to use an approximate form outside regions of its validity. In a few cases a graphical representation may be necessary. This usually occurs close to transition points, etc.

Table 1

Some Useful Representations for Thermophysical Properties, P, as a Function of Absolute Temperature, T

Eq. No.	
1	$P = A + BT$
2	$P = A + BT + CT^2$
3	$P = A + BT + CT^2 + DT^3$
4	$\ell n\ P = A + B/T$
5	$\ell n\ P = A + B/T + C/T^2$
6	$P = \sqrt{T}/[A + B/T \cdot \exp(-C/T)]$
7	$P = \sqrt{T}/(A + B/T)$
8	$P = \sqrt{T}/(A + B/T + C/T^2)$
9	$P = \sqrt{T}/(A + B/T + C/T^2 + D/T^3)$
10	$\ell n\ P = A + B/T + CT^2 + DT^3$
11	$P = \sqrt{T}/(A + BT + CT^2)$
12	$P = A + BT + CT^2 + DT^3 + ET^4$
13	$\ell n\ P = A + B\ \ell n\ T$
14	$P = aT^s$

In addition to these semiempirical or empirical representations, a more theoretical approach should be taken whenever feasible. This has generally been restricted to the dilute gas phase. One convenient region for applying theoretical models is that of the dilute gas at high temperature, where the graph on page 566 of (11) predicts a variation with the 2/3rds power of absolute temperature in viscosity and thermal conductivity for the Lennard-Jones 6-12 potential. Since the publication of (11), a considerable amount of effort has gone into extending the 6-12 potential into an m-6 and then m-6-8 model, where the m is a variable replacing the 12, the 8 being explained in (20).

Simple models, like $P = aT^s$ (Eq. 14), are very useful, as referred to on pages 565 and 566 of (11). Vargaftik (21) and others make frequent use of functionals like eqs. (13) and (14) over large temperature ranges with apparently good accuracy. The question of the possible relationship between "s" and the "m" of the potential is of some interest. This relates to the question of fitting the second-virial coefficient data to, say, an m-6-8 model and using the parameters to calculate transport properties. The fact that m and s are related is demonstrated in Table 2. An approximate graph for the collision integral Ω_{22} is shown in Figure 1, while Figures 2 and 3 plot values of $\log_{10}$ a and n as functions of m. An example

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[1] Care should be taken not to confuse the much more recent (19) organization of an American "National Engineering Laboratory" with the same-named British one.

Table 2

Values of a, n in $\Omega_{22} = aT^{*n}$ for m-6 Potentials

m	Log a	-n	Note	m	Log a	-n	Note
8	0.1087	0.211	b	16	0.0527	0.119	b
9	0.09648	0.1912	a	18	0.04601	0.1072	a
10	0.0863	0.175	b	20	0.0414	0.097	b
12	0.07183	0.1523	a	21	0.03944	0.0936	a
14	0.0609	0.134	b	24	0.03295	0.0823	a
15	0.05841	0.1270	a	30	0.02558	0.0668	a

Notes:

a. Deduced from tabulation (67).
b. Approximate, from Figures 2 and 3.

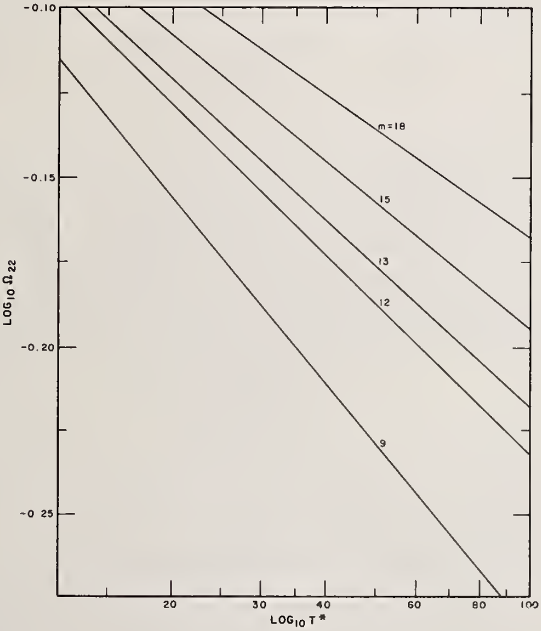

Figure 1. $\text{Log}_{10}\ \Omega_{22}$ versus $\log_{10}\ T^*$ for m-6 Potentials

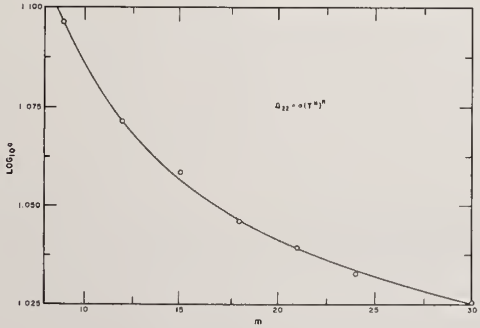

Figure 2. Variation of $\log_{10}$ a with m

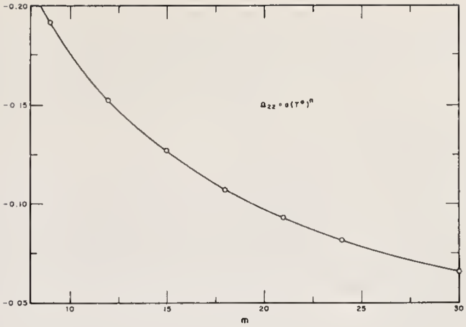

Figure 3. Variation of n with m

of the use of this approach has been given by the author elsewhere (22) in the evaluation of the high temperature thermal conductivity of krypton. This will be elaborated upon in the material on this property below.

THERMAL CONDUCTIVITY

Saturated Liquid

Figure 4 provides a schematic of the variation of thermal conductivity with temperature for a fluid. If one starts heating a liquid at the normal melting point ($T = T_m$), in general[2] the thermal conductivity decreases. Many correlations and analyses in the literature have suggested that the decrease is linear with increasing temperature so that one traces out the path ABC. The variation eventually becomes more rapid according to the simple description and one follows the curve CD to the critical point X. For the saturated vapor, far less information is available in the literature. Increasing temperature has been hypothesized to result in a curve from $T = T_m$ along E to X, again according to the simple description.

The extensive Engineering Science Data Unit correlation activity (23) originally used the simple Riedel (24) equation

$$k_L = A\ [1 + 20/3\ (1 - T_r)^{2/3}] \qquad (15)$$

to represent the variation of thermal conductivity of a liquid, k_L, with reduced temperature, T_r, where A is a numerical constant to allow for the choice of arbitrary units and T_r is the actual temperature, T, divided by the critical temperature, T_c, of the fluid. At low temperatures, $T_R \ll 1$, the variation predicted by eq. (15) is almost indistinguishable from a linear variation. More recently, a correlation at the National Engineering Laboratory (25) used a more complex expression

$$k_L = A\,[1 + B\,(1 - T_r)^{1/3} + C\,(1 - T_r)^{2/3} + D\,(1 - T_r)] \qquad (16)$$

Missenard (26) and the author (27) found that the thermal conductivities for chemically similar substances converged at one point, assuming a linear dependence on temperature. By careful analysis, values could be estimated to a moderately good degree of precision using this technique. More detailed analyses

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[2] A few exceptions occur, the most prominent being hydrogen and water.

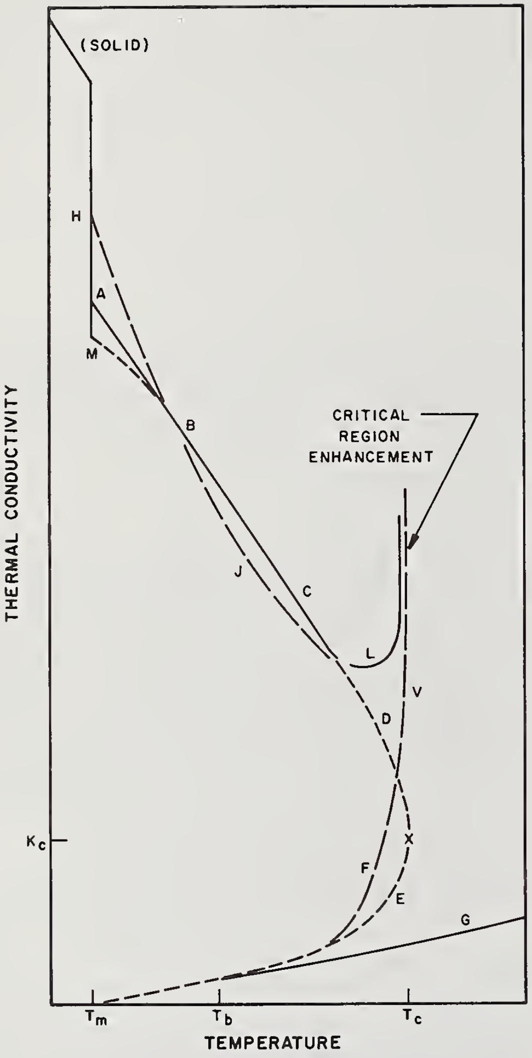

Figure 4. Schematic Thermal Conductivity-Temperature Graph

of such substances have been made. As stated by Reid et al. (28), "there is no scarcity of estimation techniques to calculate the thermal conductivity of a pure liquid. Almost all are empirical and, with only limited examination, some may appear more accurate than they are." Three of what they consider to be the best are then reviewed. The first, that of Robbins and Kingrea (29), has been widely used and predicts that

$$k_L = \frac{0.088 - 4.94 \cdot 10^{-3} H}{H_{vb}/T_b + R \ln (273/T_b)} \left(\frac{0.55}{T_r}\right)^N C_p \rho^{4/3} \qquad (17)$$

where the thermal conductivity of the liquid, k_L, is related to parameters H and N dependent upon structure and density; H_{vb} is the enthalpy of vaporization at the normal boiling point, T_b; C_p and ρ are the specific heat and density of the liquid and T_r is the reduced temperature, T/T_c, where T_c is the critical temperature. "Rarely did the errors exceed ten percent . . . but the testing was invariably carried out for $0.5 \le T_r \le 0.7$" (28). The second, a combined Sato-Riedel et al. correlation, predicts (24,28)

$$k_L = \frac{a}{\sqrt{M}} \cdot \frac{3 + 20\,(1 - T_r)^{2/3}}{3 + 20\,(1 - T_{r_b})^{2/3}} \qquad (18)$$

where the "a" depends on the unit choice for k_L, M is the molecular weight, and the T_r and T_{r_b} are, respectively, T/T_c and T_b/T_c, where T_b is the normal boiling point temperature. For this choice, "the errors noted vary widely" (28). The third, based on Missenard (26), predicts that

$$k_L = k_{L_o} \frac{3 + 20\,(1 - T_r)^{2/3}}{3 + 20\,(1 - 273/T_c)^{2/3}} \qquad (19)$$

The values predicted were generally too large. Reid et al. then made recommendations as to which of these equations should be used, the choice depending on temperature, substance, available data, etc. For reduced temperatures above $T_r \le 0.8$, a generalized correlation for the gaseous state (see below) was suggested. A thorough comparison of the efficiency of 26 equations to represent values for 12 liquids has since appeared (30). These authors recommend eq. (17) and also a further equation by Scheffy and Johnson (31).

$$k_L = a \frac{1 - 0.00126\,(T - T_m)}{T_m^{0.216}\, M^{0.3}} \qquad (20)$$

where T_m is the melting temperature, and a is a variable constant depending on unit choice. Some other equations were also recommended.

All the above refers to the saturated liquid state. The same Reid et al. source (3) compares two correlations of pressure, those of Lenoir (32), which basically graphically relate two values of conductivity to two values of reduced temperature and pressure, and Missenard (26), which relates the augmentation due to the pressure to the reduced pressure, and says that the correlations are equivalent. This suggests that an analytic form such as

$$k(P,T) = k(\text{sat. } T)\,[1 + f(P_r, T_r) \cdot P_r^n] \qquad (21)$$

where the f represents a function which can be tabulated in terms of both variables and n is a constant [suggested as 0.7 according to (26)], could possibly be used as a basis for a bivariate least mean squares fit.

Equations 15, 16, 18, 19, and 21 all imply that a functional relationship exists between k and T_r, with certain varying parameters. A systematic evaluation of these forms could be useful, although the lack of high experimental precision for a sufficiently varied collection of substances will probably result in uncertainty in the conclusions therefrom. More serious is the complete lack of allowance in all the above for special effects, such as the following:

Pre-Melting. The variation of thermal conductivity with temperature close to the melting point is suggested as becoming nonlinear (33), the curve appearing like MB. Physically, this is suggested as being due to the formation of cybotactic groups. However, a few substances appear to exhibit the opposite effect, following a curve more like HBJ.

Critical Region. The thermal conductivity does not approach a value k_c at $T = T_c$ for the saturated states but, instead, the liquid curve follows path L and the vapor curve path V, both curves showing a tendency to approach a very high or infinite value at or slightly above the critical temperature. In analysis of experimental data, one could suggest that extra care be taken with all data within ten percent of the critical temperature for pressures from one half to twice critical, although the attainment of some theoretical predictions (34) may only be realized in a very much more restricted region around the critical point. The formulation according to these predictions results in an equation of the form

$$\lambda(\rho,T) = \lambda(0,T) + \lambda_{id}(\rho,T) + kT^2 K_T F(T_r - 1,\ \rho_r - 1)\ (\partial P/\partial T)_\rho^{\,2}/(6\pi\mu\xi) \qquad (22)$$[3]

where the value at density ρ and temperature T depends on a background function (id) and on a critical excess function that depends on the compressibility K_T, the viscosity, μ, as well as a friction factor ξ and an empirical function F of reduced temperature and density. A detailed numerical formulation of thermal conductivity using a simplified version of eq.(22) is the calculation by Watson of the properties of Refrigerant 12 (35). The values so obtained do show a systematic difference with experiment (36).

Radiation. Completely neglected in all the above discussions is the possibility of energy absorption in the fluid, either preferential or total. This effect is a strongly varying function of the chemical structure of the fluids, some fluids absorbing none and some absorbing much of the energy. The effect is also a function of specimen thickness for any finite thicknesses (37). Hence, the implication is that the thermal conductivity definition should be written Watts per meter squared (area of specimen), per meter (thickness), per degrees Kelvin, and not in the usual form with specimen thickness also being cited.

Decomposition. While the normal elements and diatomic compounds are usually fairly stable, the higher molecular weight organic compounds are only one of many classes of complex structured molecules which decompose with increasing temperature. The usual experimental evidence for this is in an augmentation of the thermal conductivity, as the lighter fragments can carry energy more rapidly. But theoretical estimates of such decomposition are scarce.

Saturated Vapor

Except for a few well-known fluids, values for the thermal conductivity of the saturated vapor phase are lacking in the literature. Two principal approaches to their estimation were made. The first was to use the generalized correlation method for diatomic fluids, even in cases where the molecular complexity was of higher order and to adjust the curve to merge with the dilute gas values at the normal boiling point and/or also with pseudo-critical values. The second was to use the Liley (38) correlation

$$\Delta k = k(\text{Sat. Liq.}, T) - k(\text{Sat. Vapor}, T) = aL(T) \qquad (23)$$

which relates the thermal conductivities of the liquid and vapor phases at a given temperature T to the enthalpy of vaporization, or latent heat, L(T), of the fluid. As stated by Liley, this method cannot be expected to extend over a large interval away from the critical point, so it was used to produce values near the critical point and a smooth curve extrapolation was then used to obtain values down to the normal boiling point value determined from the dilute gas values. Thus, a graph of Δk versus L should be linear near the origin, the origin, of course, being the critical point, where $L = 0$. Figures 5-7 (38), and 8 (39) show that the linearity does apply near the origin, i.e., that eq. (23) is a valid representation. After these figures were prepared, superposition revealed almost exact coincidence for the oxygen and nitrogen graphs. The possibility of a corresponding states correlation of k with L thus exists. Furthermore, the regular variation in the slopes of the Δk versus L graphs for refrigerants of a common series is

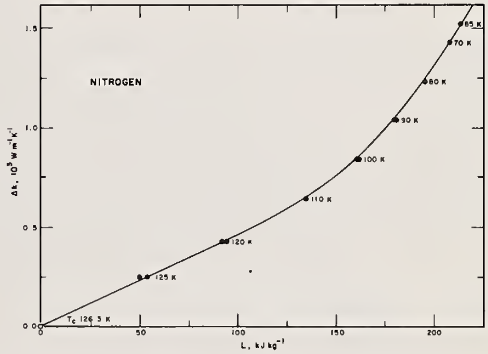

Figure 5. Variation of Δk with L for Nitrogen

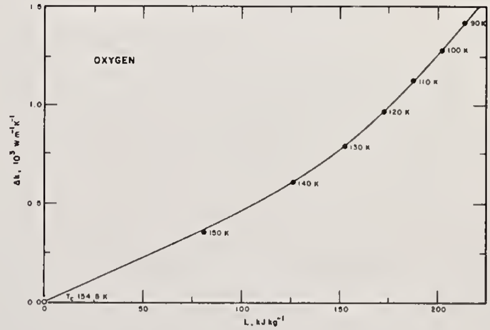

Figure 6. Variation of Δk with L for Oxygen

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[3] In eq. (22) only, the symbol λ is used to denote thermal conductivity to avoid confusion with the Boltzmann constant, k.

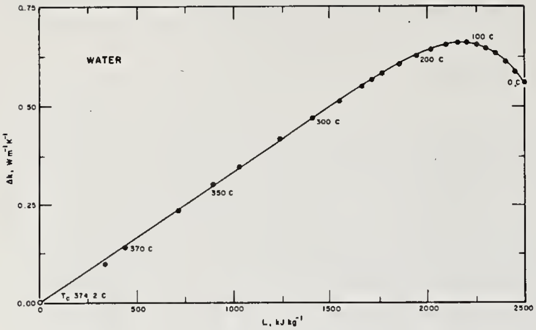

Figure 7. Variation of Δk with L for Water

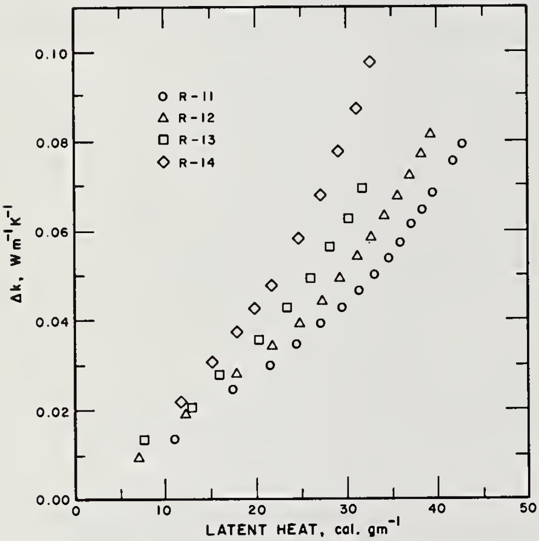

Figure 8. Variation of Δk with L for R11, R12, R13, and R14

a useful check of the inter-consistency of the various thermal conductivity values presented in the respective tables. One or more polynomial fits were usually able to represent the saturated vapor values. The uncertainty in such values is usually estimated at ten percent or less, a figure felt to be entirely characteristic of the present-day uncertainty in most measurements and tabulations.

Dilute Gas Phase. The thermal conductivity of a gas contains, in addition to the translational motion, the effect of the internal degrees of freedom which manifests itself in the Eucken correction. A detailed calculation of thermal conductivity of a gas requires calculation of viscosity, diffusion coefficient, internal and translational specific heat at constant volume and of relaxation time. The most thorough analysis is probably that of Mason and Monchick (40) for nonpolar polyatomic molecules. Involved in this formulation is the rotational collision number. Lack of adequate knowledge of it has hampered the application of this theory. Probably the most detailed treatment is that of Brokaw (41). A disturbing fact of an analysis of Barrales-Rienda (42) is that the trend of the experimental Eucken factor with temperature may be quite opposite to the theoretical results. While general reduced thermal conductivity versus reduced temperature correlations have been made for families of chemically similar substances by Thodos (43) and others, the more reliable approach would seem to be that of the group contribution method (44). But very real difficulties still exist in the interpretation of thermal conductivity of gases of even the simplest structure. For example, Kestin (45) could only conclude that thermal conductivity measurements of the monatomic gases were subject to "unknown systematic error." Maczek and Highton (68) also state that "Approximations to rigorous kinetic theory which provide reliable predictions for all the transport properties in monatomic gases and for viscosity and diffusion coefficients in polyatomic gases lose their usefulness when applied to heat transport in polyatomic gases . . . Formal theories of heat transport in polyatomic gases exist . . . But since there is no reliable method by which the necessary relaxation times can be measured, the accurate prediction . . . remains unachieved."

Analyses of thermal conductivity in other works has varied from a systematic calculation of viscosity, thermal conductivity (and possibly other properties) based on molecular models for dilute (46) and compressed (47) fluids to a tabulation and error assessment of selected values (48) with no general attempt at correlation. In general, the approximation

$$k \simeq \frac{b\sqrt{T}}{\sigma^2\Omega(T)} \qquad (24)$$

equivalent to treating the internal energy as a perturbation to the omega function has been used. The omega functions were again approximated by a series of reciprocal temperatures, so that the above approximate form was further modified to the relations in eqs. (6-9). In some cases it was found that the trend in the values calculated from rigorous theory or from more approximate forms such as the above did not differ significantly from a linear or quadratic relation (eqs. 1,2) which were, therefore, used for simplicity[4]. The average uncertainty produced, about five percent or less, is felt to be entirely comparable to most experimental data and theoretical calculations.

Our correlational efforts have, in part, been based on the following expressions. (The ranges stated are usually the case.)

1. For saturated liquids, $T_r < 0.9\ T_c$ (22,26-28,49)

$$k_L = a - bT \qquad (25)$$

2. For saturated liquids, $T \simeq 0.9\ T_c$ (24)

$$k_L - k_c = a|T-T_c|^n \qquad (26)$$

3. For saturated vapors, $T < 0.9\ T_c$ (27)

$$k_L = a + bT + cT^2 \qquad (27)$$

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[4] No attempt was made to evaluate the effect of dissociation. While in many cases this is completely negligible up to 1000 K, instances do occur where the effect does become pronounced at much lower temperatures.

4. For saturated vapors, $T = 0.9\ T_c$ (38)

$$k_L - k_V = ah_{fg} \qquad (28)$$

where h_{fg} is the enthalpy of vaporization.

5. For dilute gas (27)

$$k = \sqrt{T}/[A + B/T + C/T^2 + D/T^3] \qquad (29)$$

6. For dilute gas (22)

$$k/k_o = (T/T_o)^n \qquad (30)$$

where the zero state is usually 273.15 K.

7. For the three regions saturated liquid, saturated vapor, and dilute gas (22,28,49,50)

$$k_r = f(P_r, T_r) \qquad (31)$$

where the f refers to a generalized correlation.

VISCOSITY[5]

This is a transport property in which the internal degrees of freedom do not play a significant part. The procedures adopted parallel that for thermal conductivity so the following account can be made very concise.

Liquids

The most common relationship for expressing the variation of liquid viscosity with temperature is the logarithmic equation (eq. 4 of Table 1). Equations given as eqs. (5) and (10) were also occasionally utilized in cases where eq. (4) did not yield satisfactory agreement with the experimental data and/or did not extend over a sufficiently wide temperature range.

Close to the critical temperature, the dependence of liquid viscosity with temperature has often been represented merely by a graph or by a generalized reduced correlation, again usually in graphical form. References (27,28,50) may be found helpful as sources of additional information. We have found it convenient to represent values close to the critical point by equations of simple polynomial type (eqs. 1-3 of Table 1). An appreciable range of temperature usually exists over which the polynomial fits merge smoothly with the logarithmic. Uncertainties of five to ten percent are quite common and are entirely representative of the rather unsatisfactory state of the art for this property and phase.

Saturated Vapor

In some cases the viscosity of the saturated vapor was related to that of the dilute gas by a density function

$$\mu_{\text{sat vap}} = \mu_{\text{dilute gas}} + f(\rho) \qquad (32)$$

where the $f(\rho)$ is a polynomial or a graphical representation. The particular representation most commonly used was that of Jossi et al. (51). Density values were selected from sources considered most reliable. Values for the viscosity of the saturated vapor so obtained could invariably be represented by a polynomial (eqs. 2 or 3 of Table 1), and have an uncertainty of ten percent or thereabouts.

Gases

Equation (24) for thermal conductivity is an even more valid approximation for viscosity in the form

$$\mu \simeq \frac{a\sqrt{T}}{\sigma^2 \Omega(T)} \qquad (33)$$

Many empirical forms have been suggested to portray the actual dependence of Ω on T. Over a sufficiently limited temperature range, the omega function can often be represented as a polynomial in 1/T, so that eqs. (7-9) result. Equations (6) and (11) represent two other approximating functions. For a temperature range of several hundred degrees, eq. (9) found to invariably be able to represent the input viscosity values to within a few percent.

SPECIFIC HEAT AT CONSTANT PRESSURE

Specific heat is a thermodynamic, and not a transport, property and as such can, in principle, be calculated from the partition function. This, in practice, requires a knowledge of the equation of state. Study of these is a considerable effort. The procedure adopted was merely to compare values calculated by different equations with experimental values, and to attempt a rational analysis of the assembly so obtained.

Liquids

Either a single cubic polynomial (fitted from about the normal boiling point up to about 90% of the critical temperature) or two cubic polynomials (fitted separately to about the lower two-thirds and the upper one-third of this range) was able to represent to within several percent the specific heat of most substances studied. The few exceptions include the immediate vicinity of the critical temperature, for which graphical methods were used. Both for liquids and saturated vapors the distinction between C_p and C_{sat}, as expressed by the equation

$$C_p - C_{sat} = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P_s}{dT}\right) \qquad (34)$$

should be kept in mind.

Saturated Vapor

Our usual procedure has thus been to estimate specific heat from the enthalpy temperature variation along isobars, and then to extrapolate these values to saturation conditions if the available tables did not provide saturation data. While the accuracy so obtained has usually been of the order of five percent, two restrictions have been kept in mind. The first is that this accuracy is not secured close to the critical temperature, at which the specific heat becomes infinite. Secondly, the estimates are predicated upon the accuracy of the enthalpy data. Since, usually, the latter are derived from equation of state data, our procedure is thus essentially that of deriving specific heats from an equation of state. The fact that specific heats are related to the pressure-volume-temperature data by a function containing the second derivative of volume implies that the uncertainty in the specific heat will probably never be less than one percent except in the few cases where the fluid and the temperature range are technologically important and experimentally accessible for direct measurement.

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[5] The remarks on viscosity which follow refer to work sponsored at CINDAS. The reader may also be interested to note a separate, independent work (69).

Dilute Gas State

For zero pressure values, the results of statistical mechanical calculations within the last 20 years or so usually prove to be reasonably self-consistent where more than one calculation is available and enable a table of values to be prepared frequently to within a 1% uncertainty. The values can invariably be represented over quite large temperature ranges by cubic polynomials in temperature, i.e., eq. (3) of Table 1. A few exceptions have been found where the molecular structure is sufficiently complex that corrections for anharmonicity, etc., are significant. The ultimate accuracy obtainable thus decreases steadily with increasing complexity of the molecule. The representation of specific heat values by a cubic polynomial is sufficiently well known that no examples are felt to be necessary here.

Real Gas State

For the real gas state (i.e., for values at atmospheric pressure), two approaches have been used. By treating the available experimental and tabular information as a set, values of the specific heat were derived, again using a cubic polynomial as the interpolation device. In some cases, inconsistencies between the ideal and atmospheric pressure values were detected and have pointed up the need for further evaluation, almost invariably found to occur in the atmospheric pressure values.

PRANDTL NUMBER

The Prandtl number combines the three preceding properties. It has, until recently, received only scant analysis due largely to lack of information on the thermal conductivity. One exception was the correlation of Codegone (52,53) some 25 years ago. With the increasing need for and knowledge of thermophysical properties the situation has improved. The collection of all three constituent properties for 38 substances (27) enabled a more up-to-date evaluation of the Prandtl number to be made (54). Figure 9 is a simplified version of that appearing in the original publications (54) and shows the general way in which the Prandtl number is expected to vary with reduced temperature, $T_r = T/T_c$, for any liquid. As stated in the original publications, the preliminary analysis there presented could be improved, particularly for the saturated vapor and dilute gas states.

OTHER PROPERTIES

Similar to the Prandtl number other properties exist which are various functions of constituent properties. Three of particular interest in heat transfer applications are the kinematic viscosity,

$$\nu = \mu/\rho \qquad (35)$$

(where ρ is the density)

thermal diffusivity,

$$\alpha = k/(\rho\, C_p) \qquad (36)$$

and convective transfer

$$\text{convective transfer} = g\beta/\nu^2 \qquad (37)$$

where $\beta = 1/v\cdot(\partial v/\partial T)_p$. Another combination extensively reviewed by the author in an early work (55) is the Eucken factor,

$$f = k/(\mu C_v) \qquad (38)$$

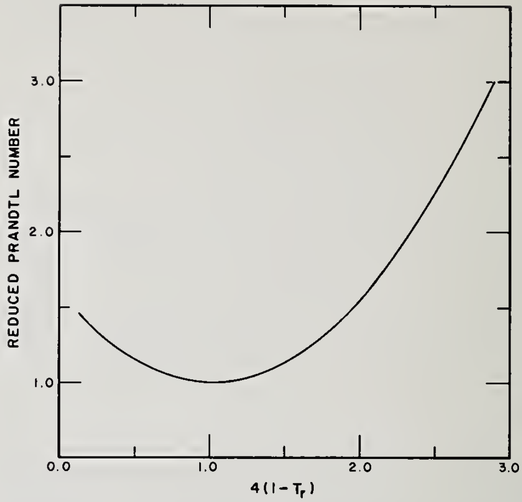

Figure 9. Reduced Prandtl Number versus Reduced Temperature Graph for Liquids

While the ability of any given intermolecular potential function to represent the thermophysical properties of a substance is an open question - a subject that is mentioned in the recommendations for further work below - in many cases it is desirable to know the intermolecular potential parameters for a certain potential so that one can use that potential to calculate the properties desired. While a few extensive tables of inter-molecular potential parameters are available (56), the thought occurred that some relationships might exist between the parameters and the position of a substance in a chemical series or group of series. This was made the subject of a thesis study (57) later published (58) where the conclusion was reached that the parameters could indeed be related to the position of the substance in a chemical series.

RECOMMENDATIONS FOR FUTURE WORK

1. The recommendations of an ad-hoc group of specialists both for the compilation of critically evaluated data and for the reporting of experimental thermal conductivity measurements (59) seem to have merit. Instances still occur in a disturbingly large number where such a consistent program is not followed. This work is again listed here in the hope that it will become more widely known and that it may be developed for other properties.

2. The growth of data banks, data units, data centers, etc. raises both hopes and fears. The hopes include that of making values of at least reasonable accuracy available very rapidly to users needing such values for design, etc. The fears include those that entry to these facilities may become prohibitively expensive for a thorough evaluation of different data and that access may also become restricted to certain groups only, denying their use to the scientific community at large. An exact parallel seems to exist here with the problem of copyright and the printed word. Study of those problems is recommended.

3. The very considerable amount of work required (60) in order to obtain a potential which exactly represents the data for a dilute monatomic gas leads one to suspect that the labor may be prohibitive for a real and complex gas and even more so for saturation states. The development of semiempirical functionals - maybe like our eqs. (1-14,24-31) - with parameters that vary regularly with chemical series and, if possible, groups of series should be of great help to (a) persons who only require that the functionals give values of reasonable accuracy, (b) persons who would use the parameters to estimate properties for so far untabulated substances, and (c) compilers of data banks.

4. The work of Klein et al. (61) on the ability of an intermolecular potential to represent pairs of properties has been followed by some studies (62) where more properties are included. It is suggested here that some other properties such as the Prandtl number and the Eucken factor could also be used and the properties contained within these could also suggest further quantities to be considered.

5. Despite the widely accepted conclusion that the principle of corresponding states fails to predict accurately enough the properties of any substance it is felt that for the more complex substances, and more so for mixtures, the principle is still capable of utilization, and it is suggested that study of such quantities as the acentric factor (63) be continued so that predictions of reasonable accuracy can be made.

6. A disturbingly unknown effect in moderately dense gas to saturation conditions is the effect of association. Only for a few substances such as steam does this seem to have received much attention.

7. Many instances (64) are available where a lack of sufficiently accurate knowledge of thermophysical properties is pointed out. Here I would just like to mention the surprising uncertainty in the thermal conductivity of air, in the dilute (65) and dissociated (66) gaseous state.

8. The establishment of a critically evaluated data base of international recognition for the common substances is recommended so that the analyses suggested in some of the preceding items may be processed and not be vitiated by later discovery of an unsatisfactory base choice.

ACKNOWLEDGMENT

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These papers were presented at a meeting of the American Society of Mechanical Engineers. The meeting session addressed the role of the accuracy of thermophysical properties data in a number of applications areas. The areas covered included aerospace sciences where such data have played a central role for a number of years, geosciences where first steps are being taken toward using accuracy in describing systems in terms of thermophysical properties. Also included were a discussion of the economic value of accuracy in the chemical process industry, a description of the role of data centers, and a description of several high quality data compilations. An example of a specific problem in the design of a heat exchanger for geothermal applications was also presented with the design uncertainties produced by data in accuracies illustrated.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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